

SYMPOSIUM B

Computational Approaches to Predicting the Optical Properties of Materials

November 30 – December 2, 1999

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Symposium Support
Silicon Graphics Inc. (SGI)

**Proceedings published as Volume 579
of the Materials Research Society
Symposium Proceedings Series.**

* Invited paper

SESSION B1:
Chair: Steven G. Louie
Tuesday Morning, November 30, 1999
Room 209 (H)

8:30 AM *B1.1

PHOTOLUMINESCENCE UPCONVERSION SPECTROSCOPY: A NEW TECHNIQUE TO STUDY TYPE II BAND-OFFSETS AT SEMICONDUCTOR HETERO-JUNCTIONS. P.Y. Yu, Department of Physics, University of California, Berkeley, and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA; G. Martinez, J. Zeman, Grenoble High Magnetic Field Laboratory, MPI-FKF/CNRS, Grenoble, FRANCE; and K. Uchida, Department of Communications and Systems, The University of Electro-Communications, Tokyo, JAPAN.

Photoluminescence upconversion is the phenomenon in which a sample emits photons with energy higher than that of the excitation photon. This effect has been observed in many materials including rare earth ions doped in insulating hosts and semiconductor heterostructures without using high power lasers as the excitation source. Recently this effect has been observed also in partially CuPt ordered GaInP epilayers grown on GaAs substrates. Using the fact that the pressure coefficient of electrons in GaAs is higher than those in (GaInP we have been able to "manipulate" the band-offset at the GaInP/GaAs interface. By converting the band-offset from Type I to Type II we were able to demonstrate that the efficiency of the upconversion process is greatly enhanced by a Type II band-offset. Furthermore, by using the magnetic length of the electrons as a "yardstick" with nm resolution we have been able to determine the size of Type II domains in GaInP near the interface. By combining high pressure and high magnetic field measurements we were able to show how the Type II domains increase in size under high pressure. Acknowledgments: Research at Berkeley was supported by the DOE through contract DE-AC03-76SF00098, The Grenoble High Magnetic Field Laboratory is "Laboratoire conventionné à l'UJF et l'INPG de Grenoble", JZ acknowledges partial support from the grant ERBCHGECT 930034 of the European Commission, Grant 202/96/0021 from the Grant Agency of the Czech Republic and Grant A1010809 of the Academy of Sciences of the Czech Republic. We also like to acknowledge collaborations with Z.P. Su, K.L. Teo, and S. Julian.

9:00 AM *B1.2

COMPARISON BETWEEN THEORETICALLY AND EXPERIMENTALLY DETERMINED OPTICAL SPECTRA OF TETRAHEDRAL SEMICONDUCTORS. Manuel Cardona, Max-Planck-Institut für Festkörperforschung, Stuttgart, GERMANY.

The state of the art of *ab initio* optical constants calculations, as discussed in this symposium, has reached a high degree of sophistication in the past few years. Nevertheless extant calculations apply only to electronic effects for a rigid lattice, disregarding electron-phonon interaction effects which are present even at $T = 0$. To minimize such problems, calculations should, at least, be compared with measurements at $T = 0$. Recent measurements with different isotopic masses have led to information on zero-point renormalization of electronic states making possible, in principle, the elimination of electron-phonon self-energies from the optical spectra measured at room temperature. Comparison of theoretical with experimental spectra leads sometimes to discrepancies that must be attributed to inadequacies in the computational codes. Such state-of-the-art codes are rather cumbersome and have been only applied to simple crystals (mostly tetrahedral semiconductors). They have not yet been used for the calculation of spectra related to higher order phenomena, such as nonlinear susceptibilities, piezo-optic functions, and Raman tensors. In these cases, semiempirical calculations of various degrees of sophistication, including sometimes analytical expressions, can be used to interpret experimental data. Semiempirical methods can also be used to calculate the effect of electron-phonon interaction on the optical spectra (as observed through the dependence of optical spectra on temperature and isotopic masses). Examples of calculations of the spectral dependence of piezo-optical functions and Raman tensors will be presented.

9:30 AM B1.3

CORRELATED MAGNETOEXCITONS IN SEMICONDUCTOR QUANTUM DOTS AT FINITE TEMPERATURE. D.J. Dean, M.R. Strayer, Physics Division, Oak Ridge National Laboratory, Oak Ridge, TN; J.C. Wells, Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN.

We describe computational methods for the theoretical study of explicit correlations beyond the mean-field in excitons confined in semiconductor quantum dots in terms of the Auxiliary-Field Monte Carlo (AFMC) method [1]. Using AFMC, the many-body problem is formulated as a Feynman path-integral at finite temperatures and evaluated to numerical precision. This approach is ideally suited for

implementation on high-performance parallel computers. Our strategy is to generate a set of mean-field states via the Hartree-Fock method for use as a basis for the AFMC calculations. Response functions are calculated at finite temperature to study the effects of exciton-carrier and exciton-exciton correlation. As an application, we compute the exciton spectrum, specific heat, and the critical temperature for the symmetry-breaking phase transition in two-dimensional quantum dots. [1] S.E. Koonin, D.J. Dean, and K. Langanke, Phys. Rep. **278**, 1 (1997).

9:45 AM B1.4

DENSITY FUNCTIONAL STUDY OF ZnGeP₂ AND CdGeAs₂ ELECTRONIC STRUCTURE UNDER HYDROSTATIC PRESSURE. Peter Zapol, Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL.

The ternary semiconductor compounds ZnGeP₂ and CdGeAs₂ are nonlinear optical materials which are particularly promising for parametric laser applications. CdGeAs₂ has a direct band gap while the pseudodirect nature of the band gap in ZnGeP₂ remains an open question. It has long been known that the pressure coefficients of forbidden energy gaps in chalcopyrites are dependent on the nature of the band gap. Crystals with pseudodirect gaps have a small positively or negatively sloped absorption edge while direct gap chalcopyrites such as CdGeAs₂ have a large positive slope. We performed density functional calculations using Gaussian orbital basis sets for CdGeAs₂ and ZnGeP₂ crystals. Structural parameters were optimized for several different unit cell volume values. Total energy vs volume dependencies were used to obtain equations of state. Energies of the top states in the valence band and the bottom states in the conduction band at T, Γ and N points were calculated to be linear functions of volume. Pressure coefficients of forbidden gaps were derived from these results and compared to experimental data.

10:30 AM *B1.5

PSEUDOPOTENTIALS AND OPTICAL PROPERTIES. Marvin L. Cohen, University of California at Berkeley, Dept of Physics, and Lawrence Berkeley National Laboratory, Materials Sciences Division, Berkeley, CA.

In the 1960's and 1970's the basic problem of explaining the optical properties of semiconductors in the visible and UV was essentially solved using semi-empirical pseudopotentials. A worldwide theoretical-experimental collaboration focused on interpreting optical structure in terms of interband transitions. The electronic band structures and response functions for reflectivity, absorption, photoemission, and modulated reflectivity experiments were determined using the EPM (empirical pseudopotential method). The results for dozens of semiconductors illustrated not only the power of the method, but also supplied useful data and yielded general interpretations of electronic properties. The semi-empirical approach gave reliable electronic density maps and slowly evolved into a first-principles method. This evolution and the origins and applications of the methods will be described.

11:00 AM B1.6

APPLICATION OF THE TIME-DEPENDENT LOCAL DENSITY APPROXIMATION TO THE OPTICAL PROPERTIES OF ATOMS AND CLUSTERS. Igor Vasiliev, Serdar Ogut, and James R. Chelikowsky, Department of Chemical Engineering and Materials Science, University of Minnesota and Minnesota Supercomputing Institute, Minneapolis, MN.

Ab initio excitation energies and photoabsorption spectra of atoms, metallic and semiconductor clusters are computed within the time-dependent local density approximation (TDLDA). The TDLDA formalism is implemented entirely in real space. Our calculations demonstrate that TDLDA technique is accurate, and when applied to clusters, is more efficient than alternative methods. In all cases considered, we find the calculated optical spectra and photoabsorption gaps to be in good agreement with available experimental data. For gallium arsenide clusters our calculations predict clearly distinguishable spectra for clusters with different structures, which may help to identify isomers. The calculated spectra for clusters exhibit long absorption tails extending deep into the region of the lower transition energies. Such behavior can be attributed to the existence of free surfaces in clusters.

11:15 AM B1.7

RESPONSE OF SEMICONDUCTORS AND FULLERENES TO ULTRASHORT AND ULTRA-INTENSE LASER PULSES. Traian Dumitrica, Ben Torralva and Roland E. Allen, Texas A&M Univ., Dept. of Physics, College Station, TX.

The interaction of matter with fast intense laser pulses is a current frontier of science. This talk will emphasize semiconductors and fullerenes, with some discussion of other molecules. We have

performed simulations which show in detail how both electrons and atoms respond to fast intense laser pulses (with durations of order 10-100 femtoseconds and intensities of order 1-10 terawatts per square centimeter). Above a threshold intensity, which results in promotion of about 10% of the electrons to the conduction band for GaAs, or 15% for Si, the semiconductor lattice is destabilized and the band gap collapses to zero. The threshold is approximately the same for GaAs and Si at a photon energy of 2 eV, because Si has stronger bonding but a higher population of excited electrons. We have also performed simulations of the response of C₆₀ and other fullerenes. We observe a symmetric excitation of electrons which softens the intramolecular bonding. As a result, there is a vibrational excitation which is almost purely in the breathing mode at low temperature. At the highest fluence for which the molecule remains intact, the vibrational amplitude is very large, with the diameter of the molecule oscillating between about 7.2 and 8.8 Angstroms. Still higher fluences produce photofragmentation, with the evolution of carbon dimers. The technique employed in the simulations is tight-binding electron-ion dynamics: Using a time-dependent Peierls substitution, one can treat the coupling of electrons to an arbitrarily strong radiation field without the need for any additional parameters. The atomic dynamics is solved with the velocity Verlet algorithm, and the electron dynamics with a Cayley algorithm. Both the time-dependent dielectric function $\epsilon(\omega)$ and the time-dependent second-order susceptibility $\chi^{(2)}(\omega)$ are monitored during a simulation for the semiconductors, and the results are in good agreement with the experimental observations of these quantities.

11:30 AM *B1.8

CRITICAL MICROSCOPIC PROCESSES IN SEMICONDUCTOR LASERS. M.S. Hybertsen, M.A. Alam, G.A. Baraff and R.K. Smith, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Operation of semiconductor laser diodes with multiple quantum wells in the active region depends on several critical microscopic processes. These include capture of carriers into the quantum wells, cooling of the injected carriers, non-radiative recombination of carriers in the quantum wells and the optical gain in the quantum wells which leads to stimulated emission. Each of these processes presents a fundamental challenge for theoretical analysis. Furthermore, experiments probe a non-trivial combination of these processes. An integrated laser simulator has been developed which includes carrier transport, quantum mechanical treatment of the quantum wells and the optical field in a self consistent analysis of the laser diode. The simulator allows direct comparison to experimental data and analysis of the impact of the various microscopic processes on the operation of the laser diode. For example, an accurate model for the optical gain, including a proper treatment of the broadening, must be combined with the details of the transport of carriers through the multiple quantum well region to understand the measured optical spectra.

SESSION B2:

Chair: Eric L. Shirley
Tuesday Afternoon, November 30, 1999
Room 209 (H)

1:30 PM *B2.1

OPTICAL SPECTRA OF SURFACES AND POLYMERS FROM FIRST PRINCIPLES. Michael Rohlfing, Universität Münster, Institut für Theoretische Physik II, Münster, GERMANY.

We present a novel approach of calculating the optical excitations of semiconducting systems from first principles [1]. To this end, we first solve Dyson's equation for the one-particle Green's function, yielding the quasiparticle excitations of the system. The electronic self-energy operator is calculated within the GW approximation. Thereafter, we solve the Bethe-Salpeter equation for the two-particle Green's function of coupled electron-hole pairs, fully including the electron-hole interaction. This allows us to investigate both bound excitons and resonant electron-hole excitations and to evaluate the entire optical spectrum. We employ this technique to investigate the optical spectra of low-dimensional systems [2]. In the case of conducting polymers, we show that the electron-hole interaction dramatically alters the absorption spectrum which is dominated by exciton states at energies below the fundamental band gap. The analysis of the corresponding electron-hole wave function yields detailed insight in the spatial correlation between the electron and the hole. In the case of the Si(111)-(2x1) surface, the differential reflectivity spectrum is dominated by a surface exciton formed from the pi-bonded surface states. The excitonic binding energy is more than one order of magnitude larger than in bulk Si. [1] M. Rohlfing and S. G. Louie, Phys. Rev. Lett. 81, 2312 (1998). [2] M. Rohlfing and S. G. Louie, Phys. Rev. Lett. 82, 1959 (1999).

2:00 PM *B2.2

AB INITIO CALCULATIONS OF RESPONSE PROPERTIES INCLUDING THE ELECTRON-HOLE INTERACTION.

Lucia Reining, Valerio Olevano, Stefan Albrecht, Madeleine Meyer, Laboratoire des Solides Irradiés, Ecole Polytechnique, Palaiseau, FRANCE; Rodolfo Del Sole, Giovanni Onida, INFN, Dip. di Fisica dell'Università Tor Vergata, Roma, ITALY.

We discuss the current status of a computational approach which allows to evaluate the dielectric matrix, and hence electronic excitations like optical properties, including excitonic effects^{1,2}. We present recent numerical developments and discuss the points which might be critical in practical applications. We will present recent applications of the method, focussing our interest on several oxides. These are materials where the experimental data yielding the electronic bandstructure in a more direct way, like photoemission, are relatively rare compared to available absorption spectra. It is therefore crucial to go towards a quantitative description of those spectra. We will show how this can be achieved, and how the ab initio calculations can yield additional information, like e.g. the localisation of the electron-hole pair.

¹ G. Onida et al, Phys. Rev. Lett. 75, 818 (1995); S. Albrecht et al, Phys. Rev. B 55, 10278 (1997); Phys. Rev. Lett. 80, 4510 (1998)

² Similar approaches are also used in L.X. Benedict et al, Phys. Rev. B 57, R9385 (1998); Phys. Rev. Lett. 80, 4514 (1998); and M. Rohlfing and S.G. Louie, Phys. Rev. Lett. 80, 3320 (1998); Phys. Rev. Lett. 81, 2312 (1998); Phys. Rev. Lett. 82, 1959 (1999).

2:30 PM B2.3

PHOTOABSORPTION OF OXYGEN DEFICIENT DEFECTS IN SILICATE AND GERMANOSILICATE GLASSES.

Krishnan Raghavachari, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

We have investigated the structural and electronic properties of oxygen deficient defects in silicate and germanosilicate glasses by ab initio quantum chemical studies using a cluster approach. In particular, the photoabsorption and photoluminescence properties of several competing defect models have been evaluated using accurate coupled cluster calculations. The performance of methods such as gradient-corrected density functional theory for the accurate evaluation of electronic excited states is assessed. The influence of the basis set and cluster size on the calculated electronic properties is explored. The effect of Ge on the relative thermodynamic stabilities of the defects is examined. Careful comparisons are performed with the known experimental information on the photoabsorption and subsequent photoemissions in silicate and germanosilicate glasses.

2:45 PM B2.4

QUASIPARTICLE EXCITATIONS, EXCITONS, AND OPTICAL ABSORPTION IN ALPHA QUARTZ. Eric Chang, Michael Rohlfing, and Steven G. Louie, Univ of California at Berkeley, Berkeley, CA.

We have investigated the optical absorption spectrum of SiO₂ using a first-principles approach, including quasiparticle self energy and electron-hole interaction effects. The quasiparticle band structure of crystalline SiO₂ in the alpha quartz phase is calculated within the GW approximation, and the optical properties are obtained by solving the Bethe-Salpeter equation for the excitonic spectrum and wavefunctions. We discover features qualitatively different from those of Effective Mass Model in these optical excitations, which reveal a rich structure in the spatial and resonance character of the excitonic states. The optical absorption spectrum in an energy range of 0-25 eV is calculated, and very good agreement with experiment is obtained. We compare the 2-particle results computed using wavefunctions and spectrum obtained from the Bethe-Salpeter equation to the one-particle interband transition results computed ignoring electron-hole interaction, and identify which peaks in the absorption are attributable to excitons and which to interband transitions.

3:30 PM *B2.5

THE ELECTRON-HOLE INTERACTION AND LINEAR OPTICAL CONSTANTS. Lorin X. Benedict, LLNL, Livermore, CA.

The attractive electron-hole interaction has an important effect on the linear optical constants of most materials. I will highlight its importance by discussing three topics in the theory of optical properties: 1) a time-dependent picture of optical absorption which helps to explain the relative strength of excitonic effects in different systems; 2) the polarization dependence of the optical constants of wurtzite GaN and AlN; and 3) ongoing work to extend present computational approaches to highly excited electron systems, in an effort to understand the results of short-pulsed pump-probe laser experiments.

4:00 PM B2.6

COMPUTATIONAL ALCHEMY APPROACH TO ALLOY

The first principles computational alchemy method is used to calculate the electronic band structure of isovalent semiconductor alloys. Starting from the virtual crystal approximation (VCA), the Kohn Sham eigen energies and quasiparticle corrections are computed within a primitive cell. The chemical substitution and bond relaxation effects are then treated by expansion out of VCA via density functional perturbation theory. The Kohn Sham eigen energies of alloys are computed by directly applying perturbations to the Kohn Sham Hamiltonian. The deviations of the quasiparticle corrections to band structure from their virtual crystal values are also examined using perturbed orbital wavefunctions as input. This approach can be used in conjunction with the special quasirandom structure method for alloy properties. It is particularly useful in cases where it may be desirable to sample multiple chemical configurations (e.g., in quaternary alloys). Comparison of our results with supercell calculations will be presented, and the limitations of this approach will be discussed.

4:15 PM B2.7

THEORETICAL APPROACHES TO SURFACE SECOND HARMONIC GENERATION. J. Mejia, Bernardo Mendoza, Centro de Investigaciones en Optica, León-México, M. Palumbo and R. Del Sole, Rome University II, Leon GTO, MEXICO.

We apply ab-initio methods and the semiempirical tight binding approach, to calculate the second harmonic generation at various surfaces of centrosymmetric semiconductors. We show that both methods give qualitative similar results. Also, we compare with the available experimental results investigated so far, and show an excellent agreement.

SESSION B3:

Chair: James R. Chelikowsky
Wednesday Morning, December 1, 1999
Room 209 (H)

8:30 AM *B3.1

OPTICAL PROPERTIES OF SILICON QUANTUM DOTS: SURFACE AND BULK ELECTRONIC STATES.

Philippe M. Fauchet, University of Rochester, Dept of Electrical and Computer Engineering, Rochester, NY.

The optical properties of direct-gap semiconductor quantum dots have been fully characterized and can be explained satisfactorily by theory. In contrast, the optical properties of silicon quantum dots are still controversial despite nearly ten years of work on porous silicon and other nanoscale silicon materials. In this presentation, we report experiments that establish how the photoluminescence of these objects is affected by the quantum dot size and the choice of the surface bonds. These results are compared to theoretical calculations that provide a microscopic understanding of the electronic states that exist in and on those dots.

9:00 AM *B3.2

OPTICAL PROPERTIES OF SILICON NANOCRYSTALS: A FIRST PRINCIPLES STUDY. Serdar Ogut, Department of Chemical Engineering and Materials Science, Minnesota Supercomputing Institute, University of Minnesota, Minneapolis, MN.

Ab initio quasiparticle gaps, self-energy corrections, exciton Coulomb energies, and optical gaps of Si nanocrystals are calculated using the higher-order finite difference pseudopotential method¹. The calculations are performed in real space on hydrogen-passivated Si clusters with diameters up to Å (> 1000 atoms). Different computational techniques, such as total energy differences from density functional theory within the local density approximation (LDA) and optical spectra using time-dependent LDA², are utilized to make systematic comparisons with experimental data. We show that the size-dependent self-energy correction is enhanced substantially compared to bulk, and quantum confinement and reduced electronic screening result in appreciable excitonic Coulomb energies. Calculated optical gaps are in very good agreement with absorption data from Si nanocrystallites.

¹ S. Ogut, J.R. Chelikowsky, and S.G. Louie, Phys. Rev. Lett. **79**, 1770 (1997).

² I. Vasiliev, S. Ogut, and J.R. Chelikowsky, Phys. Rev. Lett. **82**, 1919 (1999).

9:30 AM B3.3

TIME-DEPENDENT EXCITON CORRELATIONS IN NANOSCALE QUANTUM DOT. Lars Jonsson, Ohio State Univ, Dept Physics, Columbus, OH.

In nanoscale quantum dots, subpicosecond laser pulses can induce and probe strong time-dependent Coulomb correlations between confined electrons and holes. Correlation dynamics for one or two electron-hole pairs driven by both interband and intraband lasers can be simulated by numerical solution of the time-dependent Schrödinger equation within a configuration-interaction description. For example, Coulomb correlations of two electrons and two light holes in a 5x25x25 nm³ GaAs quantum dot yield strong oscillations in the luminescence. Pure correlation effects are revealed by a carefully chosen sequence of three circularly polarized subpicosecond laser pulses. For this case, the Coulomb and electron-laser matrix elements were calculated within the effective-mass approximation with infinite potential walls. For a quantum dot with an internal tunnelling barrier that splits the energy levels on the 10 meV scale, correlation effects couple the interband and intraband optical response. Work in progress aims at more realistic geometries, finite outer potential walls, and better description of the band structure, using real-space methods, multi-band models, and tight-binding Hamiltonians. With the help of 'dynamic state selection', simulation times can be reduced by a factor of 5-10. Dynamic state selection allows the computer, by generic selection criteria, to use only those determinants that are momentarily most important. This approach is especially useful in multi-pulse simulations where the coupled determinants belong to different classes at different times.

Supported by NSF, NCSA and OSC.

9:45 AM B3.4

THE ORIGIN AND NATURE OF STABLE ULTRAVIOLET TO RED LIGHT EMISSION FROM SILICON NANOCRYSTALS.

Howard W.H. Lee, Gildardo R. Delgado, Lawrence Livermore National Laboratory, Livermore, CA; Peter A. Thielen, University of California at Davis, Dept of Applied Science, Livermore, CA; Susan M. Kauzlarich, Chung Sung Yang and Daniel Mayeri, University of California at Davis, Dept of Chemistry, Davis, CA.

We observe intense and stable size-dependent luminescence from Si nanocrystals that can be continuously tuned from the ultraviolet to the red, and we clarify the origin and nature of this light emission. These Si nanocrystals have surfaces terminated with either silicon oxide or organic alkyl groups. Nanocrystals with different surface terminations exhibit similar optical properties, indicating luminescence from the Si nanocrystalline core. The luminescence mechanism can be separated into quantum confined and non-quantum confined contributions. Monitoring this photoluminescence (PL) produces shifts in the photoluminescence excitation (PLE) spectra that indicate size-dependent energy gaps in agreement with pseudopotential and tight binding calculations for quantum confined Si nanocrystals. Energy levels and spectra of non-quantum confined sources should not depend on the Si core size and should not shift in this specific manner. Power-dependent PL studies confirm this. Our results show that quantum confinement in Si nanocrystals is largely responsible for the tunable emission. The quantum confined luminescence surprisingly maintains an indirect character even down to small sizes (<2 nm) as indicated by phonon replicas in resonantly excited PL and by phonon absorption and emission in the PLE spectra. Oxide-terminated nanocrystals also show visible luminescence from non-quantum confined sources such as traps that are defects in the surface oxide layer. This occurs in the red (1.7 ~ 1.8 eV), green (2.5 eV), and blue-green (2.7 eV). It is size-independent and may be mistaken for quantum confined luminescence. Non-quantum confined mechanisms that give visible emission underscore the caution required for the interpretation of visible light emission from nanostructured Si. Nanocrystals terminated with organic alkyl groups show only quantum confined luminescence indicating the complete and defect-free nature of the alkyl surface termination. Work at LLNL was performed under the auspices of the US DoE by Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

10:30 AM *B3.5

EXCITATION SPECTRA IN THE TIME-DEPENDENT DENSITY-FUNCTIONAL THEORY WITH GRADIENT CORRECTION. Naoto Umezawa, Susumu Saito, Department of Physics, Tokyo Institute of Technology, Tokyo, JAPAN.

Although the density-functional theory was originally devised to describe the ground-state physical properties of interacting many-electron systems, the time-dependent density-functional treatment with the local-density approximation has been applied to various systems including atoms, molecules, and clusters during the last two decades, and it is now proven to work in describing their excitation spectra with unexpectedly high accuracy. Therefore, the extension beyond the time-dependent local-density approximation is now of high importance and interest. We apply the time-dependent density-functional theory with the gradient correction having correct asymptotic behavior to K and Na clusters. We use the jellium-sphere background model which is known to work quantitatively very well for

alkali-metal clusters. Hence the system is ideal for examining the relative accuracy of the various theoretical methods for excitation spectra. It is shown that the collective excitation energies are systematically improved by the inclusion of the gradient correction.

11:00 AM B3.6

A THREE-DIMENSIONAL COMPUTER MODEL IN SIMULATING OF THE LIGHT-TRAPPING EFFECT IN POROUS SILICON. Peter T. Charbel and Jim P. Zheng, Department of Electrical Engineering, Florida A&M University and Florida State University, Tallahassee, FL.

It has been demonstrated that the porous silicon could be used to enhance the sensitivity, spectral bandwidth, and light acceptance angle of photodiodes. In an attempt to better understand the light trapping effect of porous silicon, a three-dimensional model was used to approximate the surface geometry of the porous silicon. It was found that the main contributing factor leading to such high efficiencies is the shape of the pores. The general shape they take resembles cylindrical or cone shaped sections, whose radii are in the micron range. Although there are several factors that affect the absorption of the incident light, including the wavelength of the light and optical interference, the greatest contribution came from the light trapping shape of the pore. A three-dimensional computer model of a pore was created by using Boolean geometry to remove a conic section from a tetrahedron, where the tetrahedron represents the silicon wafer and the conic section is the pore etched from the surface. By using geometrical optics and ray tracing methods, the efficiency of the modeled pore was obtained by simulating the projection of light onto the surface of the model. The simulation involved obtaining efficiencies for the porous silicon model under different conditions, including variable angles of incidence for the projected light, variable polarization of the projected light, and variable porosity of the silicon. The results of the computer simulation were compared to actual experimental results where porous silicon was tested under variable conditions of lighting and porosity. The comparison shows that the simulation gives a good approximation of the behavior of porous silicon. Although the simulation does not perfectly match actual values, it does provide the insight that the surface geometry of porous silicon is the main contributing factor to its efficiency in trapping light.

11:15 AM B3.7

HIGH-FREQUENCY DIELECTRIC RESPONSE OF DENSE AND POROUS GLASSES. E. Guilbert and J. Kieffer, Department of Materials Science and Engineering, University of Illinois, Urbana, IL.

Large-scale molecular dynamic computer simulations have been used to generate amorphous structures exhibiting a range of densities and pore structures. Atomic interaction models used in this study account for charge transfer and the dynamic polarizability of larger ions, and are designed to describe network glass formers, such as silica and boron oxide. The evaluation of the dielectric properties of these systems includes the assignment of spectral bands to atomic trajectories, as well as the establishing of correlations between meso-scale pore structures and the lower-frequency dielectric response. Finally, an attempt is made to develop continuum representations of these porous structures, which exhibit the same properties as the atomic models.

11:30 AM *B3.8

INTER-BAND SPECTROSCOPY OF CHARGE-TUNABLE QUANTUM RINGS. R.J. Warburton, C. Schäflein, D. Haft, A. Lorke and K. Karrai, Center for NanoScience, Sektion Physik LMU, Munich, GERMANY; J.M. Garcia, W. Schoenfeld and P.M. Petroff, Materials Department and QUEST, University of California-Santa Barbara, Santa Barbara, CA.

Quantum dots based on GaInAs/GaAs modulation n-doped heterostructures have been grown by molecular beam epitaxy in a field effect arrangement. Such field effect devices allow the number of electrons confined in the quantum dots to be tuned electrostatically from 0 to approximately 6 simply by using a gate potential. With such a fine level of tuneability, we have here a unique opportunity to study few electron-electron interactions in semiconductor quantum dots. In the present work, the properties of such interacting electrons are probed optically at 4.2 K by measuring the absorption and emission of excitons confined in the dots together with the stored charge. The "transmutation" from Hydrogen-like to Carbon-like quantum dots can be therefore monitored optically while sweeping the gate voltage applied on the dots. Samples were grown with two different types of confinement potentials, namely "ring-like" and "parabolic-like". We measured the excitonic emission spectra originating from a single quantum dot as a function of the number of electrons present in it. The energies and the amplitudes of the absorption and emission peaks are found to be directly correlated with the number of charges present in the dots. While the

experimental results for the parabolic-like dots are found to be very well accounted for by an analytical Hartree-Fock perturbation theory in the strong confinement limit [1] the more novel ring-like quantum dots are presently not fully understood and offer new interesting challenges. [1] R.J. Warburton et al. Phys. Rev. B58, 16 221 (1998).

SESSION B4:

Chair: Gerard Martinez
Wednesday Afternoon, December 1, 1999
Room 209 (H)

1:30 PM *B4.1

OPTICAL ABSORPTION AND INELASTIC LIFETIMES IN NOBLE METALS. A. Rubio, Dpto. Fisica Teorica, Valladolid, SPAIN; I. Campillo, J.M. Pitarke, Materia Kondentsatuaren Fisika Saila, Euskal Herriko Unibertsitatea, Bilbao, SPAIN; E. Zarate, P.M. Echenique, Materiales Fisika Saila, Euskal Herriko Unibertsitatea, San Sebastian, SPAIN.

Applications of the Time Dependent Density Functional Formalism to calculate the response of metallic and semiconducting systems to static and time-dependent electric fields are reviewed. We analyze in detail the role of the localized *d*-bands in the dynamical response of noble metals (Cu, Ag and Au). We also present new data on the inelastic lifetimes of excited electrons computed within the GW approximation. Our full band-structure calculations indicate that actual lifetimes are the result of a delicate balance between localization, density of states, screening, and Fermi-surface topology. Comparison with experiments is made and discussion for further improvements are outlined.

2:00 PM *B4.2

EFFECTS OF ELECTRON-ELECTRON INTERACTION IN MAGNETO-OPTICAL SPECTRA OF 2D SEMICONDUCTOR STRUCTURES. Marek Potemski, Grenoble High Magnetic Field Laboratory, MPI/FKF and CNRS, Grenoble, FRANCE.

In the presence of free carriers, which can be optically excited or of extrinsic origin, electron-electron interactions induce changes in the optical properties of semiconductors. These many-body interactions have lately rekindled an interest in the studies of confined electronic systems such as optically pumped and/or modulation doped quantum well structures. Two-dimensional electronic systems subjected to high magnetic fields are of particular interest, firstly due to simplified experimental conditions (discrete energy levels) and secondly due to the unique nature of electron-electron interactions in the case of fully degenerate electronic levels (quantum Hall regime). The effects attributed to many-body interactions, observed in interband magneto-optical spectra involving two-dimensional electron gas and electron-hole plasma will be discussed. Particular attention will be focused to processes of optical recombination from a two-dimensional electron gas under Landau-quantization conditions. Apparent discrepancies between experimental observations and theoretical understanding of many-body features in the optical spectra of 2D semiconductors will be underlined.

2:30 PM B4.3

OPTICAL AND TRANSPORT PROPERTIES OF METALS FROM FPLAPW CALCULATION. Kentaro Uehara, John S. Tse, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, CANADA.

The optical properties and electronic transport properties of solid are directly related to the topology of the Fermi surface. For example, plasma frequency is calculated from the surface integral of the Fermi velocity, Hall coefficient is calculated from first and second derivatives of the Fermi surface. The evaluation of those physical quantities requires accurate bandstructure on very fine k-point grid. The recent development of highly accurate electronic structure calculation method and technique of band fitting procedure enables us to explore good candidates of potential novel materials from first-principles calculation. A full-potential linearized augmented plane wave (FPLAPW) method in a framework of the density functional theory (DFT) is one of the most accurate electronic structure calculation method and it has been applied to many solid state systems such as transition metals, semi-conductors and high- T_c superconductors. Because the FPLAPW method is an all-electron method, which involves core electrons explicitly in the calculation, we can obtain X-ray absorption/emission spectra, Knight shift, dielectric tensor, plasma frequency within an accuracy of DFT. We have implemented modified SKW band interpolation scheme to the FPLAPW method and calculated the Fermi surface and its derivatives on very dense k-point grid with small computational cost. We will present the detailed analysis of the Fermi surface and results of plasma frequency, Hall coefficient and thermoelectric effect for some metals and alloys.

2:45 PM B4.4

AB INITIO OPTICAL PROPERTIES OF Cu(110) SURFACE. Patrizia Monachesi*, Rodolfo Del Sole, Giovanni Onida, Maurizia Palumbo, Tor Vergata Univ, Dept of Physics, Rome, ITALY; Rajeev Ahuja, Olle Eriksson, Uppsala Univ, Dept of Physics, Uppsala, SWEDEN. *on leave from Univ of L'Aquila, Dept of Physics, ITALY.

We present *ab initio* calculations of the optical properties of metallic surfaces. We consider the (110) clean surface of Cu for which the anisotropic surface reflectivity (RAS) has been recently measured [1]. This technique takes advantage of the anisotropy induced by a surface in an otherwise symmetric bulk lattice. With an implemented FP-LMTO code [2], we compute the optical properties, i.e., the dielectric function, and hence the RAS. We use the slab technique, including 11 atomic layers and 4 vacuum layers. The resulting RAS spectrum agrees with the experimental curve. In particular, the large peak at about 2 eV and the structures at about 4 and 5 eV found experimentally, are reproduced by the present calculations.

Considering a smaller slab of only 7 atomic layers, gives only a qualitative agreement between measured and computed RAS. We also interpret the observed RAS structures through the analysis of interband transitions among the bulk-bulk, surface-surface and bulk-surface electronic states. To our knowledge, these are the first *ab initio* calculations of optical properties of metallic surfaces.

[1] K. Stahrenberg, Th. Herrmann, N. Esser, W. Richter, to appear in *Physica Status Solidi*

[2] J. Wills, O. Eriksson, unpublished

3:30 PM *B4.5

DOPANT-INDUCED STRUCTURAL INSTABILITIES AND PERSISTENT-PHOTOCONDUCTIVITY IN SEMICONDUCTORS AND INSULATORS. D.J. Chadi, NEC Research Institute, Princeton, NJ.

Over the last decade it has become increasingly evident that many dopants commonly used in the p- and n-doping of semiconductors induce a structural bistability at an atomic level. The bistability is often accompanied by the phenomenon of persistent-photoconductivity (PPC) in which the dopant undergoes a transition from a deep state into a shallow state upon exposure to light. The ability to calculate total-energies with high accuracy has led to the identification of the two primary low energy states responsible for PPC. A review of the main results for III-V and II-VI semiconductors and in the very large band gap material CdF₂ will be given in this talk.

4:00 PM B4.6

DEFECT AND PRESSURE INDUCED EFFECTS ON OPTICAL PROPERTIES OF MOLECULAR CRYSTALS. Maija M. Kuklja, A. Barry Kunz, Electrical Engineering Department, Michigan Technological University, Houghton, MI.

Molecular crystals belong to a wide class of the technologically important materials. Most of them are composed of poly-atomic molecules having a complicated structure. In the present study, the defect- and surface-induced effects on the optical band gap of a solid C₃H₆N₆O₆ (RDX) were investigated by means of a first-principle, quantum-chemical method. The Hartree-Fock calculation scheme (CRYSTAL95) combined with the many-body perturbation-theory (LOPAS) permits us to simulate the atomic and electronic structure of a series of lattice defects in RDX such as a molecular vacancy, a vacancy dimer, an edge dislocation, a nano-crack, and a (210) surface. As a result, we can predict how their presence in the crystal will affect its optical properties. The effect of high external pressure on the electrical and optical properties of the material is also studied. It is well known that some materials lose their transparency under high compression. This phenomena, for example, is characteristic for detonation initiation in high explosive solids, which undergo an electronic phase transition. In our study, the critical pressure for the insulator-metal phase transition in RDX is predicted and analyzed for both the defect-free material and the solid containing defects. The obtained results compared with the relevant experimental data and are of great practical importance, in particular, our conclusions provide useful insights for the control of sensitivity of explosive crystals to detonation initiation.

4:15 PM B4.7

FIRST-PRINCIPLES CALCULATIONS OF OPTICAL PROPERTIES OF SURFACES. Cecilia Noguez, Instituto de Fisica, Universidad Nacional Autonoma de Mexico, Mexico DF, MEXICO.

We developed a first-principles method to calculate optical properties of surfaces starting from their fully relaxed atomic configurations. We present a method that employs a localized pseudoatomic orbital basis set. The approach allows dealing with inhomogeneous systems, like surfaces, consisting of up to several hundred atoms per unit cell. We

present results for GaN surfaces, in terms of their calculated optical surface dielectric response function. We compare the results in with semiempirical tight-binding calculations and experimental measurements.

SESSION B5: POSTER SESSION

Chair: James R. Chelikowsky
Wednesday Evening, December 1, 1999
8:00 P.M.

Exhibition Hall D (H)

B5.1

COMPUTATION OF THE POROUS Si DIELECTRIC FUNCTION IN THE SUPERCELL MODEL AND COMPARISON WITH EXPERIMENT. Julia Taguena-Martinez, Yuri Rubo, CIE-UNAM, MEXICO; Miguel Cruz, ESIME-IPN, Mexico City, MEXICO; Marcela Beltran, Chumin Wang, IIM-UNAM, Mexico City, MEXICO.

We present the results for the imaginary part of the dielectric function of porous silicon, which were obtained with the tight-binding 128-atom supercell model [1] for porosities 64%, 70%, and 76%. For the 70% porosity case we have also considered a few different pore morphologies. The onset of the absorption depends substantially on porosity and morphology, which also affect the width of the main absorption peak. In particular, the width increases noticeably for low-symmetry pores. Since the real samples have pores of different sizes and shapes, we have performed a statistical average over these parameters to compare with the experimental data [2]. References: [1] M. Cruz *et al.*, *Phys. Rev. B* **59**,15381 (1999). [2] N. Koshida *et al.*, *Appl. Phys. Lett.* **63**, 2774 (1993).

B5.2

MINIBAND STRUCTURE AND OPTICAL TRANSITIONS IN A SUPERLATTICE WITH ELECTRON QUASI-LOCALIZED STATES IN UNIT CELL. Alexey Dmitriev, Vladislav Makeyev, Moscow State Univ, Dept of Low Temperature Physics, Moscow, RUSSIA.

We studied theoretically the miniband spectrum and optical transitions in a superlattice with quasi-localized (resonant) electron states in unit cell. We considered the superlattice or multi-quantum well structure (MQWS) with unit cell that contains a well, the main barrier separating the wells in the neighboring cells, and two additional semi-transparent barriers at both sides of the well. The additional δ -barriers form resonant electron states at energies above the main barriers.

A dispersion relation and carrier wave functions were found for such superlattices, and their miniband structure was calculated. Near energies of the resonant states the electron spectrum and wave functions have specific hybrid properties where features of under- and above-barrier states are intermixed. The shape of a miniband formed by the quasi-localized states differs significantly from that of minibands consisting of barrier states.

The inter-miniband dipole matrix element and the corresponding absorption coefficient for the transitions from states of the lowest miniband were calculated. The absorption increases greatly for the transitions to vicinities of the resonances. If the energy width of the resonance exceeds the miniband width, which may happen in a long-period superlattice or MQWS, then the region of the absorption enhancement may cover several minibands. When the superlattice period tends to infinity, our results agree with those obtained by us earlier for a single quantum well with resonant states.

B5.3

DEFECT INDUCED EFFECTS ON MECHANICAL AND DIELECTRIC PROPERTIES OF YTTRIUM-ALUMINUM COMPOUNDS. Maija M. Kuklja, Electrical Engineering Department, Michigan Technological University, Houghton, MI; Institute of Chemical Physics, University of Latvia, Riga, LATVIA.

Yttrium Aluminum compounds are important materials, which technological applications range from lasers to propulsion systems. For example, the Nd³⁺ doped YAG is a well-known laser material whereas YAG:Al₂O₃ composite is found to be an ideal material for high-temperature ceramic applications. In the present study, theoretical simulations of mechanical and dielectric properties depending on basic point defects in Yttrium-Aluminum Compounds such as Perovskite (YAlO₃) and Garnet (Y₃Al₅O₁₂) crystals were performed in terms of interatomic potentials coupled with the classical shell model description of the lattice ions. A new set of potential parameters first obtained for the perfect lattice allows us to model atomic structures of different types of the intrinsic (vacancies, interstitials, antisites) and impurity (Ca²⁺, Mg²⁺, Ba²⁺, Sr²⁺, Cr³⁺, Fe³⁺, Nd³⁺, Si⁴⁺) point defects. Using the calculated defect formation energies we obtain activation energies for defect reactions, from which we determine the most probable defect processes in Yttrium-Aluminum perovskite and garnet. We found that in both

compounds the antisite disorder is more favorable than the Frenkel and Shottky-like disorder. It is shown that antisite substitution YAl_x causes a distortion in the crystalline lattice shortening the Y-O bond length whose calculated value is in excellent agreement with the EXAFS measurements. Deviations from stoichiometry were modeled by an excess of yttrium and aluminum oxides. Some other properties such as electrical conductivity induced by impurity defects, changes in elastic properties, and complex defect cluster formations as well as migration mechanisms were also considered. A comparison with the relevant experimental data is presented.

B5.4
HIGHLY REFLECTIVE MIRRORS FOR DBR APPLICATIONS OPERATING AT 1.55 μm : AlGaInAs/InP AND GaInSbAs/InP MATERIAL SYSTEMS. M. Linnik, A. Christou, Materials and Nuclear Engineering Department, University of Maryland at College Park, MD.

Theoretical optimization of the refractive indices and energy band gaps of the III-V quaternary alloys in the form $A_xB_{1-x}C_yD_{1-y}$, $A_xB_yC_{1-x-y}D$, and $AB_xC_yD_{1-x-y}$ was conducted as a function of the incident wavelength and the alloy composition. The investigation and comparison of the refractive indices of the quaternary alloys lattice matched to InP revealed two highly reflective material systems, $\text{Ga}_{0.78}\text{In}_{0.22}\text{Sb}_{0.29}\text{As}_{0.71}/\text{InP}$ and $\text{Al}_{0.05}\text{Ga}_{0.42}\text{In}_{0.53}\text{As}/\text{InP}$, which may be used as distributed Bragg reflectors lasing at 1.55 μm due to the large optical index difference they provide between alternating layers. A reflectivity of 99% can be achieved by growing only 15 pairs of AlGaInAs/InP or GaInSbAs/InP Bragg mirrors on InP substrate and taking GaInAsP as an active layer.

B5.5
ELECTRONIC STATES OF SELF-ASSEMBLED QUANTUM DOTS WITH LENS GEOMETRY: THE ROLE OF SYMMETRIES. C. Trallero-Giner, A. Hernández-Rodríguez, J. Marín-Antuña, Department of Theoretical Physics, University of Havana, CUBA; S.E. Ulloa, Department of Physics and Astronomy, Ohio University, Athens, OH.

Self-assembled semiconductor quantum dots are modeled with a geometry of lens-shape described by a spherical cap of height b and circular cross section with radius a . In an envelope function formalism, the corresponding Hamiltonian for a carrier confined in this lens geometry is mapped into an equivalent equation with semi-spherical shape. Geometrical effects on carriers energies and wavefunctions as a function of the lens height b are studied. Exact solutions are reported for the particular case of $b = a$ and a modified Rayleigh-Schrödinger perturbation theory is applied to obtain analytical expressions for the energy levels and eigenfunctions, as function of the b/a ratio. Numerical calculations are presented for confinement by an infinite hard wall. The degeneracy due to the z -component of the angular momentum m is broken for $b \neq a$. Energetic states with $m = 0$ present the most pronounced influence on $b \neq a$ case. The same behavior is observed for the eigenfunctions of the quantum dot with lens-shape symmetry. The effect of decreasing symmetry on the exciton binding energy is studied also using a numerical matrix diagonalization technique with the obtained electron and hole wavefunctions as basis set. Analytical expressions presented here can be used to estimate the sizes of actual self-assembled quantum dots. Finally, we present the role that these states play on the excitonic states and optical response of such quantum dots.

B5.6
LOCAL BASIS GW CALCULATIONS AND THE DIELECTRIC RESPONSE OF SILICON CLUSTERS. Ming Yu, Sergio E. Ulloa and David A. Drabold, Department of Physics and Astronomy and Condensed Matter and Surface Sciences Program, Ohio University, Athens, OH.

We present our progress in developing an *ab initio* computational scheme for calculation of the dielectric response function of solids, with special emphasis here in Si clusters. All calculations are carried out employing a basis of localized atomic-like orbitals and include the evaluation of quasiparticle corrections. The self-energy operator is evaluated in the GW approximation, with a full frequency dependence for the dielectric matrix. The approach is convenient and computationally optimal for the calculation of optical properties of complex systems lacking full periodicity, such as surfaces and clusters. We present here the quasiparticle energy structure for Si₂₀ and Si₆₀ clusters with structures found from full equilibration via molecular dynamical simulations. We discuss the sensitivity of the optical properties to quasiparticle corrections, and the convergence with respect to the size of the localized orbital basis. Comparisons are also made with bulk silicon calculations in the generalized pole approximation. We find that the optical gap in clusters is larger than in bulk silicon, likely the result of size quantization and structural disorder.

B5.7
INTERACTION OF MOLECULES WITH ULTRASHORT INTENSE LASER PULSES: A NONADIABATIC QUANTUM MOLECULAR DYNAMICS APPROACH. Thomas Niehaus, German Cancer Research Center, Dept of Molecular Biophysics, Heidelberg, GERMANY; Ben Torralva, Roland E. Allen, Dept of Physics, Texas A&M Univ, College Station, TX; Markus Elstner, Thomas Frauenheim, Universität-GH Paderborn, Fachbereich Physik, Theoretische Physik, Paderborn, GERMANY; Sandor Suhai, German Cancer Research Center, Dept of Molecular Biophysics, Heidelberg, GERMANY.

We present a nonadiabatic quantum molecular dynamics approach, which is suitable to study the response of large polyatomic systems to intense laser pulses. Starting from a quantum-classical Lagrangian, coupled equations of motion for electrons and ions are derived. The electronic wavefunction is propagated according to the Kohn-Sham equation of time dependent density functional theory. We implemented this scheme using a density functional based tight-binding method [1], where the necessary matrix elements are determined within a confined LCAO basis in a two-center representation. Forces on the nuclei are obtained from a generalized Ehrenfest theorem and the external radiation field is incorporated via minimal coupling, where following Graf and Vogel [2] the field dependent matrix elements may be rewritten in a numerical feasible way. Results show the dominate photoexcitation of the breathing mode in C₆₀ and the red-shift of this mode due to ultra-intense laser pulses with fluences on the order of 4.0 KJ/m². These findings agree well with pump-probe experiments on thin films recently performed by Dexheimer *et al.* [3]. [1] D. Porezag, Th. Frauenheim, Th. Kohler, G. Seifert, R. Kaschner, Phys. Rev. B **51**, 12947 (1995). [2] M. Graf and P. Vogl, Phys. Rev. B **51**, 4940 (1995). [3] S.L. Dexheimer, D.M. Mittleman, R.W. Schoenlein, W. Vreka, X.-D. Xiang, A. Zettl, and C. V. Shank, Ultrafast Phenomena VIII, Springer-Verlag, Berlin, (1993).

B5.8
IMPROVED OPTICAL PROPERTIES OF SEMICONDUCTORS USING DENSITY FUNCTIONAL THEORY. S.J. Clark and R.A. Abram, The University of Durham, Department of Physics, Science Labs, Durham, UNITED KINGDOM.

The need to make reliable simulation of optical properties of materials is becoming increasingly important and new technologies make demands for highly specialised semiconducting devices. One of the most commonly used first principles methods for calculating electronic, and therefore optical properties of materials is density functional theory. However, the major drawback of this method is that it underestimates the band gap of materials, often by up to 50%, which can be traced back to the single particle excited state Kohn-Sham orbitals and the need for a discontinuity in the exchange-correlation functional, which is not correctly described by the usual local density and generalised gradient approximations. This leads to a poor description of excited state energies which appears as an underestimate in the electronic band gap. We have performed band structure calculations on a range of semiconducting and insulating materials using a constrained excited state energy minimisation technique, combined with an exchange-correlation functional within the generalised gradient approximation which corrects for long-ranged correlation effects. This combined technique predicts band gaps to within a few percent of experimental values without any additional computational cost.

B5.9
OPTICAL AND DIELECTRIC PROPERTIES OF WURTZITE AlGaN SOLID ALLOY. Ivan Kityk, Michał J. Malachowski, Pedagogical Univ., Institute of Physics, Czestochowa, POLAND.

Calculated results for band structure of AlGa_xN solid alloy are shown. We present the solid alloy structure as a superposition of two sublattices with the appropriate weighting factors. Both the *ab initio* norm-conserving pseudo-potential (PP) and LCAO methods give essential disagreement with the experimental data. Only the appropriate correction of the norm-conserving PP method by the orthogonalized LCAO wave functions essentially stabilizes the convergence procedure. To check the reliability of the proposed method we have carried out experimental investigation of the optical functions for two representatives of the investigated wurtzite AlGa_xN solid alloys. Calculations were performed as a function of energy cutoff as well as the degree of orthogonalization of norm-conserving pseudowave function to the LCAO wavefunctions. The optical functions at zero frequency give an overestimated values comparing with the experimental data. The best agreement with the experiment can be achieved by using the orthogonalization procedure between the norm-conserving pseudowave and LCAO wavefunctions. The last ones help in understanding of the appearance of the solid alloys structure

modulations in the mentioned compounds. The spectral dependence of absorption coefficients for GaN and AlGaIn are of crucial importance. So called 'square root' law is commonly used in spite of some discrepancies with the available experimental data. The results of our calculation concerning the band structure enabled realization a numerical evaluation of spectral dependence of absorption coefficient. The results were compared with the 'square root' law as well as with the experimental data available in the literature.

B5.10

COMPUTATION OF OPTICAL PROPERTIES FOR QUANTIZED ELECTRONIC SYSTEMS. Verne L. Jacobs, Center for Computational Materials Science, Materials Science and Technology Division, Naval Research Laboratory, Washington, DC.

A density-matrix description has been developed to treat relaxation (decoherence) phenomena during resonant and non-resonant radiative transitions of quantized electronic systems, including many-electron atoms and quantum-confinement systems (e. g., semiconductor microstructures). Radiative and collisional relaxation phenomena have been treated using Liouville-space projection-operator techniques. Both time-independent (resolution-operator) and time-dependent (equation-of-motion) formulations have been developed. The self-energy operators that occur in these formulations can provide the fundamental basis for a self-consistent determination of the non-equilibrium and coherent electronic-state kinetics together with the homogeneous spectral-line shapes. This density-matrix description can be adapted for the computer simulation of electromagnetic processes. From first-principles electronic-structure calculations or from semi-empirical approaches, the parameters describing the elementary collisional and radiative interactions can be evaluated and organized into the basic data set for the application of the density-matrix description. The final product is a theoretical prediction for the linear or non-linear optical absorption or emission spectrum corresponding to a given set of values for the appropriate physical variables, such as temperatures, densities, and electric or magnetic field strengths. This work has been supported by the Department of Energy and by the Office of Naval Research.

B5.11

FIRST-PRINCIPLES CALCULATION OF OPTICAL SPECTRA FOR Cr³⁺ DOPED IN α -Al₂O₃ AND MgO. Kazuyoshi Ogasawara, Masateru Yamamoto, Takugo Ishii, Teruyasu Mizoguchi, Fumiyasu Oba, Hirohiko Adachi, Kyoto Univ, Dept of Materials Science and Engineering, Sakyo-ku, Kyoto, JAPAN; Isao Tanaka, Kyoto Univ, Dept of Energy Science and Technology, Sakyo-ku, Kyoto, JAPAN.

The multiplet structures of Cr³⁺ doped α -Al₂O₃ (α -Al₂O₃:Cr³⁺, ruby) and MgO:Cr³⁺ are calculated from first-principles using a hybridized method of the density functional theory (DFT) and the configuration interaction (CI) calculation (DFT-CI approach). In the DFT-CI approach, the single-electron orbitals are calculated by a spin-restricted density functional calculation. Then the many-electron wave functions are expressed as linear combination of the Slater determinants by diagonalizing the many-electron Hamiltonian. The effective reduction of electron-electron repulsion integrals due to electron correlation is evaluated from the consistency between the spin-unrestricted density functional calculation and the DFT-CI calculation. The structural relaxations around the impurity Cr³⁺ ions are also taken into account by static energy minimization technique using pair potentials. In the case of ruby, the intensity of the electric-dipole transition arising from the intrinsic trigonal distortion are calculated numerically using the many-electron wave functions obtained by the DFT-CI calculation. The calculated intensity qualitatively reproduced the anisotropy of the absorption spectra of ruby. In the case of MgO:Cr³⁺, there are Mg²⁺ vacancy for every two Cr³⁺ in order to satisfy the charge neutrality and there are slightly distorted sites with tetragonal or rhombic symmetry according to the position of the Mg²⁺ vacancy. The intensity of the electric-dipole transition at these distorted sites are calculated by the similar computational approach and are compared with the absorption spectra of MgO:Cr³⁺.

B5.12

THEORETICAL INVESTIGATION OF THE GEOMETRICAL AND ELECTRONIC STRUCTURES AND NONLINEAR OPTICAL HYPERPOLARIZABILITIES OF SOME FUSED HETEROCYCLIC AROMATIC COMPOUNDS. Mamoun M. Bader, Dept. of Chemistry, Penn State University, Hazleton, PA.

Results of our ab initio calculations of the geometrical and electronic structures and the NLO hyperpolarizabilities of a series of heterocyclic aromatic molecules (based on pyridine) containing different donor and acceptor groups will be presented. 15 compounds are considered in this study. The effect of geometry, type and relative positions of the substituents on the molecular properties will be discussed. Basis set dependence of the calculated parameters will also be addressed.

B5.13

PLASMON REFLECTION OF LIGHT BY CRYSTALS IN THE FRAME OF THREE-LAYER MODEL. P. Kosoboutski, T. Slysarchuk, A. Danylov, State University Lviv Polytechnic, Dept of Physics, Lviv, UKRAINE.

The theoretical study of conditions of extrema formation in plasmon reflection spectra for crystals with nondispersive layer on surface is carried out. It was determined that minimum of reflection contour $R_{13}(\omega)$ forms at frequency ω_m when wave phase shift in the layer and for reflection from internal layer-substrate interboundary equals $\varphi_{23} + \delta_s = 2\pi$, where $\delta_s = 4\pi n_s d_s / \lambda$ is wave phase shift in the layer with thickness d_s and index of refraction n_s . From the condition of phase compensation for three-layer model we obtained the relation between ω_m , δ_s and optical indices of refraction and absorption of electromagnetic wave in substrate volume:

$$\omega_m^2 \approx \frac{\omega_p^2}{\epsilon_\infty} \cos^2 \frac{\delta_s}{2}$$

where ω_p is the plasmic frequency, ϵ_∞ is the dielectric constant with nonresonance contribution of bound charge. For the case we assume, that damping factor $\gamma = 0$. As was determined, extrema position strongly depend on both angle of incidence and phase thickness of the layer on surface. The shape of phase spectrum near resonant region is investigated. If the hodograph of complex reflection coefficient r passes through origin of coordinate axes $\text{Re } \tilde{r}_{13}$ and $\text{Im } \tilde{r}_{13}$ the phase spectrum changes of S \leftrightarrow N type take place.

B5.14

THE INFLUENCE OF 5- AND 6-ATOM RINGS ON THE OPTICAL PROPERTIES OF a-SILICON NITRIDE. A CLUSTER SIMULATION. R.M. Valladares, A.G. Calles, Facultad de Ciencias, UNAM, México, D.F., MEXICO; Alexander Valladares, Ariel A. Valladares, Instituto de Investigaciones en Materiales, UNAM, México, D.F., MEXICO.

We simulate a - SiN with two types of clusters: a - Si_{21-i}N_i : H that contains 6-atom boat-type rings and a - Si_{17-i}N_i : H that contains 5-atom planar rings, where $i = 0, 1$ or 4, [1], [2]. The simulations were carried out using the DFT-LDA approximation contained in the DMol code of MSI. We report calculations of impurity levels and relate these to the size of the gap and to the optical absorption curves for each cluster. A comparison is made between the two a - SiN clusters studied to analyze the effect of the ring topology as well as to experiment. Clusters are useful to investigate the influence of specific structures or defects in amorphous materials. [1] *Optical Properties of Tetrahedral a-Carbon Nitride*, A.A. Valladares et al. To be published in Synth. Metals. [2] *Influence of 5-atom Rings on the Optical Properties of a-Carbon Nitride*, R.M. Valladares et al. To be published in Synth. Metals.

B5.15

SIMULATION OF X-RAY DIFFRACTION ON MULTILAYERS SUBJECTED TO DIFFUSION. A.G. Fedorov, Institute for Single Crystals, Condensed Molecular Films Division, Kharkov, UKRAINE.

Multilayers with great difference of electron density of alternating layers widely used in X-ray optics as dispersing elements, or X-ray mirrors. Their efficiency depends among others from interface abruptness and flatness and from stability under heavy radiation and temperature influence. The diffusion intermixing and formation of new phases on the boundaries may take place at these circumstances. Mathematical description of low angle X-ray diffraction on these structures and resulting diffraction pattern is commonly based on Fresnel equations, that supposes the presence of uniform dielectric constant by the layer and abrupt interfaces. But real multilayer may not offer such ideal rectangular profile. Usually, the way out is to approximate such smoothed profile as a set of lamella. In this work another approach is considered based on solution of Maxwell equations for layered structure with arbitrary profile of dielectric constant distribution. Solution gives the Riccati type equation for angular dependence of reflectivity R in X-ray wave range

$$\frac{dR}{dz} = -2ik_0 R \sqrt{\epsilon(z) - \sin^2 \varphi_0} + (1 - R^2) \frac{\epsilon'(z)}{4[\epsilon(z) - \sin^2 \varphi_0]} \quad (0.1)$$

where $\epsilon'(z) = d\epsilon/dz$, dielectric constant $\epsilon(z)$ in X-ray wave range defined as $\epsilon = 1 - \delta + i\gamma$ and

$$\delta = \frac{e^2}{mc^2} \frac{\lambda^2}{\pi} N_a f_1, \quad \gamma = \frac{e^2}{mc^2}$$

$\lambda^2 \frac{e^2}{\pi N_a f_2} f_1$ and f_2 - real and imaginary parts of atomic scattering factor. If we consider $\epsilon = \text{const}$, then we obtain from (1)

$$\frac{dR}{dz} = -2ik_0 R \sqrt{\epsilon - \sin^2 \varphi_0}$$

and

$$R = R_0 \exp(-2ikh_0h\sqrt{\epsilon - \sin^2\varphi_0}) \quad (0.2)$$

where h - film thickness, initial condition R_0 is the known Fresnel equation for reflection from the boundary of two media. This is just the equation (2) which is used for reflection calculations in a simple case of rectangular multilayer profile. Using (1) solved numerically with Runge-Kutta 4th order method the X-ray diffraction patterns were calculated for different conditions of profile transformations. It was shown that diffusion with different diffusion coefficients on the neighboring boundaries that leads to asymmetrical profile transformation causes reduction of some reflections and increase of another ones.

B5.16

ENERGY DISPERSION CONTOUR APPROACH TO CALCULATE OPTICAL PROPERTIES OF QUANTUM WELL STRUCTURES. T. Osotchan, W. Shi, D.H. Zhang, School of Electrical and Electronic Engineering, Nanyang Technological University, SINGAPORE.

In order to calculate optical properties i.e. dielectric function, refractive index and absorption coefficient, the evaluation of integration including ground and excited wavefunctions is required over entire k -space. The contour of energy dispersion was proposed to form the criteria to select and limit the value of \mathbf{k} in the integration. With the contour approach the integration can be determined to truncate at certain \mathbf{k} value where the weight factor of Fermi-Dirac distribution function become very small and the fraction of integration can be ignored. The approach was applied to $AlGaAs/AlAs/GaAs$ double barrier quantum well structures with 14-band $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian. By systematically modify this quantum well structure the dependence of absorption peak width was investigated in bound-to-bound and bound-to-continuous intersubband transitions. The energy dispersion contours of each involved state were illustrated in two dimensional k -space with the compositions in perpendicular and parallel directions to the interface. The calculated refractive index and absorption as a function of wavelength can be simply extracted from the contour characteristic especially at the constant Fermi energy surface.

B5.17

A METHOD OF INCORPORATING THE COMPOSITION INTO THE CALCULATION OF THE $Si K_{\beta}$ X-RAY EMISSION SPECTRUM OF THE SiO_2 - CaO BINARY GLASS BY THE DV- $X\alpha$ MOLECULAR ORBITAL CALCULATION. Masao Morishita, Koichiro Koyama, Tadayoshi Kikko, Dept of Materials Science and Engineering, Himeji Institute of Technology, Himeji, JAPAN.

$Si K_{\beta}$ X-ray emission spectra of SiO_2 - $AlCaO$ binary glasses simulated by the DV- $X\alpha$ molecular orbital calculation were compared with ones measured by EPMA. The composition of the slag has been incorporated in the calculation of the partial density of states of 3p component of Si ion. The calculated partial density of states of 3p component of Si ion as a function of the CaO content agreed well with the measured $Si K_{\beta}$ X-ray emission spectra of the 62.4mol% SiO_2 -37.6mol% CaO and 43.3mol% SiO_2 -56.7mol% CaO binary glasses. The present method was found to provide a very useful means of clarifying the change in ionic configuration of the glass with the metal oxide content, and also of understanding the concept of basicity at the same time.

B5.18

SIMULATION OF DIFFUSE LIGHT EXPOSURE OF LOW TEMPERATURE CO-FIRED CERAMIC TAPES AND THE PROBLEM OF SIDEWALL MORPHOLOGY. P. Espinoza-Vallejos, J.J. Santiago-Aviles, Univ of Pennsylvania, EE Dept, Philadelphia, PA; L. Sola-Laguna, DuPont Electronic Materials, RTP, NC.

The photo-formable Low Temperature Co-fired Ceramic Tapes is a versatile material system with great potential in the field of meso-scale (where features range from 10 micrometers to several centimeters), 3-D structures, and the packaging of silicon based MEMS. This alumina based glass-ceramic composite system is similar to the conventional LTCC tapes, except that the organic part of the binder composition includes a photo-polymer acting as a resist. This allows the transferring of arbitrary patterns to the tape by the use of the nominal tools of UV lithography. The resolution limit seems to be imposed by the diffusive nature of the light scattering within the filler alumina grains. Diffuse light scattering is a random walk phenomenon. The processing consequence of this phenomenon is the enhanced spreading of the mask diffracted light in the dimension normal to the light beam, and the subsequent undercutting upon development. We have simulated the diffusive light scattering of UV light in a photo-formable tape. We calculated the form factor $F(q)$ and the geometrical scattering factor $S(q)$. The form factor was approximated using Mie scattering and $S(q)$ using the Percus-Yevick

hard-sphere potential approximation. With the knowledge of these parameters, we numerically integrated the light diffusion equation with an extended source using the Green Function method. We experimentally measured the transport mean free path (random walk step) between scattering events. After processing the tape we have achieved features size of 70 microns in a 150 micron - thick tape. We are able to predict and control the undercut due to scattering of the light by alumina grains. The experimental verification of the model utilizes a modified version of diffuse-Transmission Spectroscopy (DTS) using the material development characteristics as a sensor. The technique involves the measurement of extinction coefficient by measuring the sample thickness as a function of energy.

B5.19

FINITE ELEMENT ANALYSIS OF 2-D DIELECTRIC WAVEGUIDES WITH HELMHOLTZ VECTOR EQUATIONS AND VIRTUAL EXTERIOR ELEMENTS. Tiejun Zheng, The GWW School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA; Nai-Keng Bao, Kin-Seng Chiang, Po-Sheun Chung, Department of Electronic Engineering, City University of Hong Kong, Kowloon, HONG KONG.

In optical devices, the vector analysis is necessary when the weak guides assumption is invalid. Since what are concerned in a optical field are its electrical field components, it is expected to get the electrical field directly in the analysis in order to achieve more precise electrical field result than looking for the magnetic field first then deriving the electrical field from the magnetic field. A finite-element-method formulation is developed on the base of the Helmholtz vector equations in terms of transverse electrical field components to characterize two-dimensional dielectric waveguides with arbitrary continuous permittivity profile. Since the dielectric waveguides analysis is sensitive to its boundary conditions, virtual exterior element iteration technique is associated with the finite element analysis to process the remote boundary condition. This technique increases both the computational efficiency and accuracy than introducing a large amount of real finite elements for the remote boundary conditions. The propagation constants and cutoff frequencies can be calculated from the resulting eigenvalues. the modal electrical field can be obtained directly from the resulting eigenvectors without any spurious solutions. Numerical results of optical fibers with the parabolic permittivity profile are presented to show the validity of this technique.

B5.20

FIBER BRAGG GRATING GROWTH SIMULATION USING AN INVERSE SCATTERING MATRIX APPROACH. Alessio Manca, Dept of Physics, Cagliari, ITALY.

Fiber Bragg gratings are playing an important role in the field of optical telecommunications and sensors. We have simulated the growth of such gratings, longitudinally written in the core of germanosilicate optical fibers by an Argon ion laser. Following a Kramer-Kronig model, absorption in the Germanium Oxygen deficient band (~240 nm) is considered to be responsible for the fibers' photosensitivity and a two photon absorption process models the dynamics of the refractive index variation. The spatial propagation of light through the grating is described by the coupled waves theory and is calculated by using the new inverse scattering matrix technique. The predicted physical properties, the reflectivity of gratings and the temporal dispersion of propagating light as a function of wavelength and input power, show that a sustained growth is possible. The scattering matrix approach has been proved a useful mean even in the case of temporal evolution with respect to previous works.

B5.21

EFFECTIVE PERMITTIVITY OF COMPOSITE COMPOSITES. Christian Brosseau, Université de Bretagne Occidentale, FRANCE; A. Beroual, A. Boudida, École Centrale de Lyon, FRANCE.

The effective electromagnetic, thermal and mechanical properties of heterogeneous media are commonly related to composition. Composite composites are entities that are important in physics and engineering and are a class of compounds actively investigated for their dielectric properties. Such systems consist of composite inclusions of multicomponent materials embedded in a matrix of a distinct material. The effects of volume fraction, permittivity, thickness, and shape of the various constituents on the complex permittivity of the heterostructures are reported. We present calculations of the complex effective permittivity for different types of composite composites, in the quasistatic approximation. We use an exact numerical technique for the evaluation of the dielectric characteristics of composite composites, arranged in a regular simple cubic lattice, which is based on the field calculation package PHID and the resolution of boundary integral equations. All internal electric multipole interactions contributing to the sharp increase of the real and imaginary parts of the effective permittivity, at the critical point where the inclusions

touch, are taken into account. The predictions of Maxwell Garnett (dipolar) theory and the effective medium approximation are in poor agreement with our numerical results. Typical results presented for stratified spheres and ellipsoids indicate that any approach based solely on the dipole approximation must fail to predict the effective permittivity of dielectric heterostructures. The results discussed give motivation for the development of careful experiments which can be used to test the numerical simulations and the processing of synthetic composite materials in which new electromagnetic properties can be obtained from the combination of several materials.

SESSION B6:
Chair: Marvin L. Cohen
Thursday Morning, December 2, 1999
Room 209 (H)

8:30 AM *B6.1

INELASTIC X-RAY SCATTERING WITH HIGH ENERGY RESOLUTION: A NEW METHOD TO STUDY THE HIGH FREQUENCY ATOM DYNAMICS IN CONDENSED MATTER.
Francesco Sette, European Synchrotron Radiation Facility, Grenoble Cedex, FRANCE.

One motivation to the development of intense and collimated synchrotron sources is the interest to exploit inelastic x-ray scattering as a novel spectroscopic probe for condensed matter. Important limitations imposed by energy resolution requirements, incident and scattered photon energy tunabilities, and photon flux have so far slowed down the development of this technique, and sometime even questioned its real possibilities. Only very recently, thanks to the construction of a new electron storage ring with unprecedented low emittance at the European Synchrotron Radiation Facility in Grenoble, and thanks to new developments of highly performing perfect crystal optics, the scenario is rapidly changing to the point that it is now possible to perform inelastic x-ray scattering measurements in the ~ 20 KeV x-ray energy region with energy resolutions tunable in the 7-1.5 meV range.

An important domain of application of the x-ray technique is the study of the high frequency dynamics in the time and length scale domains characteristic of interparticle density fluctuations. This is traditionally the domain of application of neutron inelastic scattering. When one consider systems without translational invariance, however, the neutron techniques become quite difficult and sometime impossible to use as a consequence of kinematic limitations in the relevant momentum and frequency region. This explains why there are very few coherent inelastic neutron scattering studies on disordered systems, and why there are still many open questions on the high frequency dynamics of liquids, glasses and dense fluids in general. These kinematic limitations are overcome using x-rays. Similarly, the small dimensions of the x-ray beam favour experiments on small sample, eventually in extreme thermodynamic conditions as high pressure.

The present contribution will give an overview on the x-ray inelastic scattering techniques to study of inter-particles dynamics, and it will present some of the results obtained so far on the new instrument, operating in Grenoble since the last five years.

9:00 AM *B6.2

SCREENED-EXCHANGE LDA METHODS FOR BULK, FILMS AND SUPERLATTICES. R. Asahi, W. Mannstadt and A.J. Freeman, Department of Physics and Astronomy, Northwestern University, Evanston, IL.

We have developed new screened-exchange LDA (sX-LDA) methods for films and superlattices (FLM/SL) in order to calculate self-consistent electronic structure for both occupied and unoccupied states without adjustable parameters. Considering non-uniform charge densities and local-field effects in the z direction for FLM/SL, we employed nonlocal Thomas-Fermi wave vectors to define the screened exchange interaction. Three methods, for bulk, superlattice, and film, are implemented in the full-potential linearized augmented plane wave (FLAPW) method. For bulk Si, Ge, InSb and GaAs, we have presented results of the electronic structures and optical properties obtained with self-consistent eigenfunctions (Phys. Rev. B **59** 7486 (1999)). The results for wurtzite GaN, as a test case, showed that the superlattice method gives as accurate a band structure (including the band gaps and the binding energy of the semicore d states) as the bulk one, and that both methods yield identical band structure in the limit of a uniform density used as input to the dielectric function. We have also established the film method by comparing results of a single Si monolayer slab with those of a superslab treated as a superlattice including vacuum region. The methods demonstrated here have a wide range of applicability, including possible direct determinations of the band offsets at both conduction and valence bands, and of the Schottky barrier formed by adsorbed metal layers.

Supported by the NSF (through the NU Materials Research Center) and Toyota Central R&D Laboratories, Inc.

9:30 AM B6.3

NONLOCAL POLARIZABILITIES AND THE AB INITIO CALCULATION OF SURFACE OPTICAL PROPERTIES OF GaAs (110). C.M.J. Wijers, Computational Optics, Faculty of Applied Physics, University of Twente, Enschede, THE NETHERLANDS; P.L. de Boeij, Theoretical Chemistry, Materials Science Centre, University of Groningen, Groningen, THE NETHERLANDS.

We demonstrate that the description of the optical reflectance anisotropy of GaAs (110) requires a complete microscopic treatment of both surface and bulk, which is feasible in the discrete cellular method. This method is an extension of standard discrete dipole calculations and accounts for nonlocality in the electrodynamic and quantummechanical interactions through the use of both real space local fields and ab-initio nonlocal polarizabilities. The nonlocal polarizabilities are obtained from the ab initio full potential, total energy LDA-BAND package. The discrete dipole part of the calculation requires more normal modes than the usual Fresnel ones, to represent the bulk. The results are in excellent agreement with experiment and we show that the anisotropy is surface induced.

9:45 AM B6.4

SEMIEMPIRICAL SELF CONSISTENT FIELD MODELING OF THE Ce^{+3} 4F-5D ENERGY LEVELS IN SOLID STATE LUMINESCENT MATERIALS. Philip D. Rack, Rochester Institute of Technology, Department of Microelectronic Engineering, Rochester, NY; Ted A. O'Brien, Michael C. Zerner, University of Florida, Quantum Theory Project, Gainesville, FL; Paul H. Holloway, University of Florida, Department of Materials Science and Engineering, Gainesville, FL.

Rare earth doped semiconductors are known to be efficient luminescent materials. In particular, SrS and $Sr_xCa_{1-x}Ga_2S_4$ doped with Ce^{+3} have recently been explored as efficient blue cathodoluminescent and electroluminescent materials for flat panel display applications. The blue emission in these materials is due to Ce^{+3} 5d-4f transitions, and the transition energies are sensitive to the local chemistry of the Ce^{+3} . To understand the effect that the local chemistry has on the Ce^{+3} 4f-5d emission spectrum, we used a self-consistent-field configuration interaction (SCF/CI) model to calculate the electronic spectrum of the Ce^{+3} ion embedded in a cluster representation of the semiconductor lattice. The effects of changing nearest neighbor anions and cations have been modeled and are in excellent agreement with the experimental spectroscopy. In this presentation we will discuss the SCF/CI model and the cluster geometry used to represent the solid lattice. In addition, we will compare the calculated and experimental Ce^{+3} 4f-5d emission spectra for different materials, and correlate the spectral changes to an analysis of atomic orbital electron populations.

10:30 AM B6.5

THEORETICAL AND EXPERIMENTAL ANALYSIS OF THE LOWER DIELECTRIC CONSTANT OF FLUORINATED SILICA. Alex Demkov, Ran Liu, Stefan Zollner, Dennis Werho, Mike Kottke, Rich Gregory, Semiconductor Product Sector, Motorola, Inc., Mesa, AZ; Matt Angyal, Semiconductor Product Sector, Motorola, Inc., Austin, TX; L.C. McIntyre Jr., M.D. Ashbaugh Department of Physics, University of Arizona, Tucson, AZ.

The fluorinated silica (FTEOS) is known to have the dielectric constant in the range of 3 to 3.5 that is significantly lower than that of the fluorine free material (4). The reasons behind the reduction of the dielectric constant are not very well understood and are somewhat controversial. It is not known exactly whether the electronic or ionic contributions to the overall screening is being diminished upon the fluorine doping. To shed more light on this phenomenon we have studied FTEOS both theoretically with ab-initio modeling and experimentally with various characterization techniques. Far-IR transmission and spectroscopic ellipsometry measurements gave us the electronic and ionic contributions to the susceptibility. Nuclear reaction analysis was used to measure fluorine composition. XPS and Auger experiments provided the information on the atomic structure of the film. We use a large cell of cristobalite to model fluorinated silica theoretically. The ground state geometry is obtained via the energy minimization. Two types of Fluorine have been found; a bridging fluorine acts just as an oxygen atom, and forms two Si-F bonds (0.159 nm, and 0.162 nm). In addition, we find a terminal fluorine atom that forms only one bond to Si (0.152 nm). As a result a nano-pore forms in the simulation cell. Analysis of the Si-O-Si bond angle distribution in the cell shows that even though the average angle of 147° is still very similar to that in fluorine free cristobalite angles as low as 120° and as high as 170° are introduced to the system. We calculate the vibrational density of states at the Gamma point, and analyzed the modes using the inverse participation ratio

(IPR) (IPR indicates localized modes). We find a strongly localized mode at 935 cm^{-1} , this vibration involves the terminal fluorine. The calculated frequency agrees well with the 938 cm^{-1} value measured by far-IR transmission, and with the Si-F stretch reported in the literature [1,2]. The Auger experiments indicate that mobile F species leaves the sample if the Al cap is removed. We suggest that it is the terminal fluorine that is mobile. This suggestion is confirmed by the reduction of the 938 cm^{-1} mode. We compute the electronic and the ionic susceptibilities for models with various fluorine concentrations. The effect of fluorination on the dielectric constant will be discussed. [1] K. Kim, D. H. Kwon, G. Nallapati, and G. S. Lee, *J. Vac. Sci. Technol.* **A16**, 1509 (1998). [2] G. Lucovsky and H. Yang, *J. Vac. Sci. Technol.* **A15**, 1509 (1997).

10:45 AM B6.6

PREDICTING NONLINEAR OPTICAL PROPERTIES OF DELOCALIZED CHARGE STATES IN POLENYLIC CHROMOPHORES AND DENDRIMERS. Carl Dirk, University of Texas-El Paso, Dept of Chemistry, El Paso, TX; Charles Spangler, El Hadj Elandaloussi, Luis Madrigal, Montana State University, Dept of Chemistry and Biochemistry, Optical Technology Center, Bozeman, MT.

While there have been numerous approaches to calculation and prediction of optical properties of organic nonlinear (NLO) optical chromophores, most have focused on linear quasi-1d conjugated chromophores. Thus electron delocalization is confined to the linear chain backbone. Recently, we have utilized a new calculational approach at the AM-1 level to predicting the optical properties of polaronic radical-cations and bipolaronic dications formed from neutral polyenes with various mesomerically interactive substituent groups. The order of magnitude of the calculated second hyperpolarizability, γ , and the stabilization ordering by the substituents compares very favorably with experimental results. We have now extended this approach to predicting charge delocalization and stabilization in quasi-2d and -3d dendrimer structures. As the progression from 1d to 3d structures is examined, extremely large enhancement of the bipolaronic γ is predicted, to the extent that these new materials may be the most nonlinear organic materials yet envisioned. Recent experimental evidence from two-photon absorption measurements on these dendrimers suggest that this prediction may indeed be correct, and thus create new paradigms for the design of third-order NLO materials.

11:00 AM *B6.7

POLYMERIC CARBON DIOXIDE. Choong-Shik Yoo, Lawrence Livermore National Laboratory, Livermore, CA.

Application of high-pressure strongly perturbs chemical bonds, electronic and crystal structures, thermal and mechanical properties, and reactivities of solids. These pressure induced changes, however, often occur in systematic ways, providing new routes for designing and synthesizing novel materials with advanced optical and mechanical properties. As an example, we present the phase transition of carbon dioxide from a molecular phase to a novel extended polymeric phase that can be viewed as being similar to its heavier periodic assemblage SiO_2 .

Synthesis of polymeric carbon dioxide has long been of interest to many chemists and materials scientists. The attempts, however, had not been successful for many decades, until very recently we discovered the polymeric phase of CO_2 -V at high pressures and temperatures. In this paper, we describe this polymerization together with the stability, structure, and mechanical and optical properties of CO_2 -V. Our optical and x-ray results indicate that CO_2 -V is optically non-linear, generating the second harmonic of Nd: YLF laser at 527 nm and is also likely superhard similar to cubic-boron nitride or diamond. CO_2 -V is made of CO_4 tetrahedra, analogous to SiO_2 polymorphs, and is quenchable at ambient temperature at pressures above 1 GPa.

* This work has been done in collaboration with H. Cynn, F. Gygi, G. Galli, V. Iota, C. Mailhot at LLNL; M.F. Nicol at UNLV; S. Carlson, D. Hausermann at ESRF and has been performed under the auspices of the US Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

11:30 AM B6.8

RECENT ADVANCES IN *AB INITIO* TIME-DEPENDENT HARTREE-FOCK THEORY AND THEIR APPLICATIONS TO PREDICT OPTICAL PROPERTIES OF SEMICONDUCTOR NANOCCLUSERS. Shashi P. Karna and Prakashan P. Korambath*, US Air Force Research Laboratory, Space Vehicles Directorate, Kirtland AFB, NM. *National Research Council Resident Associate

Ab initio time-dependent Hartree-Fock (TDHF) theory provides a simple and straightforward means to model optical materials. However, until recently, its application has been limited to molecular systems containing less than half a dozen atoms. Two recent

advancements in the TDHF theory have, however, made it a technique of choice for modeling nanoscale optical materials from first-principles. The first advancement has been the introduction of the $(2n+1)$ rule of the perturbation theory in coupled Hartree-Fock (CHF) solution of TDHF equations¹. This allows calculations of $(2n+1)$ th-order energy from the n th-order wavefunction, resulting in considerable savings of computational resources. The second major advancement has been the introduction of the direct approach of solving TDHF equations². In the direct-TDHF approach, the ubiquitous two-electron integrals (TEI) needed to construct Fock matrices are calculated as and when needed, thus obviating the need to store and process billions of TEI, as is done in the conventional compute-store-and-retrieve (CSR) approach. These developments also lends themselves to be easily adapted with other first-principles approaches, such as the unrestricted Hartree-Fock (UHF) for open-shell calculations³ and density functional theory⁴. In this paper, we shall review the recent advancements in the TDHF theory and demonstrate its applicability by presenting results for the linear and nonlinear optical properties of nanoclusters consisting of group III (Ga) and group V (N, P, As) atoms. From the analysis of the results and a comparison with related experimental data, the merits and the demerits of the TDHF theory in modeling optical materials will be discussed.

1. S. P. Karna and M. Dupuis, *J. Comp. Chem.*, **12**, 487 (1991).
2. S. P. Karna, *Chem. Phys. Lett.* **214**, 186 (1993).
3. S. P. Karna, *J. Chem. Phys.* **104**, 6590 (1996).
4. S. J. A. van Gisbergen, J. G. Snijders, and E. J. Barends, *Phys. Rev. Lett.* **78**, 3097 (1997).

11:45 AM B6.9

THE FIRST PRINCIPLES STUDY ON LIGHT EMITTING PROPERTIES OF SEMICONDUCTING METAL SILICIDES. Kenji Yamaguchi, Kazuki Mizushima, and Koichi Sassa, Central Research Institute, Mitsubishi Materials Corporation, Omiya, JAPAN.

Semiconducting metal silicides are potential candidates of silicon-based light emitting materials [1]. In order to carry out screening of the candidates, we calculated the oscillator strength between the valence and excited states near the band gap for such silicides as FeSi_2 , CrSi_2 , ReSi_2 , Ru_2Si_3 , OsSi , OsSi_2 , MnSi , LaSi_2 , Ir_3Si_5 , Mg_2Si , Ca_2Si , and BaSi_2 . The electronic states were obtained by the full-potential linear augmented-plane-wave method (FLAPW) [2] based on the local density approximation (LDA). The results show Ru_2Si_3 and Ca_2Si are direct gap semiconductors, while FeSi_2 , CrSi_2 , OsSi , OsSi_2 , Ir_3Si_5 , and Mg_2Si are indirect gap semiconductors. Although, in experiments, ReSi_2 , MnSi , LaSi_2 , and BaSi_2 were reported as small gap semiconductors, the underestimation of the band gaps by LDA caused the closure of the gaps. Ru_2Si_3 and Ca_2Si have direct gaps at Γ point, but the values of the oscillator strength across the gaps are evaluated to be zero. Among the indirect gap semiconducting silicides, FeSi_2 , OsSi , and OsSi_2 have several peaks and valleys facing each other near the band gap. Among the combinations of the facing peaks and valleys, we obtained the biggest value of oscillator strength 0.3 at X point for OsSi with band gap energy of 0.42 eV. [1] D. Leong, M. Harry, K. J. Reeson, and K. P. Homewood, *Nature*, **387**, 686 (1997). [2] P. Blaha, K. Schwarz, and J. Luitz, WIEN97, Vienna University of Technology, Vienna 1997.

SESSION B7:

Chair: James R. Chelikowsky
Thursday Afternoon, December 2, 1999
Room 209 (H)

1:30 PM *B7.1

FIRST-PRINCIPLES CALCULATIONS OF NONLINEAR OPTICAL RESPONSE FUNCTIONS IN SEMICONDUCTORS. Sergey N. Rashkeev and Walter R.L. Lambrecht, Case Western Reserve University, Cleveland, OH.

We discuss recent progress in calculation of nonlinear optical response functions in semiconductors. Since the work of Sipe and coworkers (*Phys. Rev. B* **48**, 11705 (1993); *ibid* **52**, 14636 (1995)) it became clear that the calculation of nonlinear optical response functions in crystals of general symmetry requires a careful distinction of pure inter-band and mixed intra-inter-band contributions in the time evolution of the electron density operator under the influence of the electromagnetic field perturbation. We present our implementation of this approach using the linearized muffin-tin orbital method and discuss its application to the calculation of second harmonic generation (SHG), the linear electro-optic (LEO) effect, and circularly polarized current injection. The importance of gap corrections beyond LDA is discussed. The relation of the second order response functions to the linear response function is illustrated and it is shown how band structure information is contained in these spectra with an example from SiC polytypes. As primary application, we discuss the SHG

coefficients of chalcopyrites of both the II-IV-V₂ and I-III-VI₂ families. We show that the decomposition in inter- and intra-inter-band contributions leads to new insights in the reasons for the high $\chi^{(2)}$ of some of these materials. We also present results for LiGaO₂, a material with high band gap and discuss its applicability to frequency conversion into the UV. Supported by NSF.

2:00 PM B7.2

FIRST-PRINCIPLES CALCULATIONS OF POSITRON ANNIHILATION IN SOLIDS. B. Barbiellini, Northeastern Univ, Dept of Physics, Boston, MA; M. Hakala, HUT, Lab of Physics, Espoo, FINLAND; R.M. Nieminen, HUT, Lab of Physics, Espoo, FINLAND; M.J. Puska, HUT, Lab of Physics, Espoo, FINLAND.

We present first-principles approaches based on the density functional theory for calculating positron states and annihilation characteristics in condensed matter. The treatment of the electron-positron correlation effects (the enhancement of the electron density at the positron with respect to the mean-field density) is shown to play a crucial role when calculating the annihilation rates. A generalized gradient approximation (GGA) takes the strong inhomogeneities of the electron density in the ion core region into account and reproduces well the experimental total annihilation rates (inverses of the positron lifetimes) by suppressing the rates given by a local density approximation (LDA). The GGA combined with an electron-state-dependent enhancement scheme gives a good description for the momentum distributions of the annihilating positron-electron pairs reproducing accurately the trends observed for deep core and uppermost d electrons in the II-VI compounds in the angular correlation (ACAR) or Doppler broadening measurements of the annihilation radiation. The reliability of the present positron lifetime and momentum density calculations yields a unique tool for defect identification in semiconductors. We will show that the identification of vacancy-impurity complexes in highly n-Type Si is a particularly successful application.

2:15 PM B7.3

Abstract Withdrawn.

3:00 PM *B7.4

SECOND-HARMONIC GENERATION IN SEMICONDUCTORS AND INSULATORS. Zachary H. Levine, NIST, Gaithersburg, MD.

Over the past several years, the calculation the nonlinear susceptibility on a nearly first-principles basis has been created more or less from scratch. The key theoretical developments were a method to correct local-density functional band gaps, and the simple recognition that fairly accurate wave functions were required for reliable work. Calculations have been carried out for a number of crystals, including cubic semiconductors, SiC polytypes, Se, quartz, and urea. One advance over an older generation class of theories — the bond charge model — occurs in understanding III-N semiconductors.

3:30 PM B7.5

Abstract Withdrawn.

3:45 PM B7.6

THE INFLUENCE OF VACANCIES ON OPTICAL PROPERTIES OF SiC NANOCRYSTALS. K.J. Plucinski, Military Univ of Technology, Electronics Dept, Warsaw, POLAND; I.V. Kityk, Institute of Physics WSP, Czestochowa, POLAND; A. Kassiba, University of Maine, LeMans, FRANCE; C. Charpentier, Univ of Maine, LeMans, FRANCE.

The origin of vacancies in SiC nanocrystals is not yet fully understood. It is important to devise a procedure for modeling such vacancies since they can significantly change the optical and electronic properties of SiC nanocrystals. This feature could broaden possibilities for new development in opto-electronic devices. Most of the procedures that we are aware of are based on an over-simplified crystalline-like approach. In the best case, the dependence of the total energy on particle size has been investigated. Most of the previous calculation approaches have been based on a simplified linear molecular orbital or on pseudopotential calculations of existing vacancy models without consideration for the surrounding atomic arrangement. A major objective of our work was to devise a model for vacancies which would make it possible to assess their influence on optical properties of SiC nanocrystals. Using a complex approach that included ab initio molecular dynamics simulation and calculations within the basis set of the norm-conserving nonlocal pseudopotential, we made calculations of the probability of a vacancy spin-polarised state occurring as a function of nanoparticle and grain sizes. The optimised structural geometry of the real interface was built on the basis of a molecular dynamics procedure with dynamics boundary conditions. Using the optimised structure obtained we thus carried out optimisation in the vicinity of the charged vacancies. We have shown a significant influence of the local geometry rearrangement on

the symmetry of the surrounding atoms. We carried out numerical estimations of the corresponding isotropic spin-polarised wavefunctions and compared the results with experimental EPR data.