

TRANSMISSION ELECTRON MICROSCOPY STUDY OF THE FUSED SILICON/DIAMOND INTERFACE

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ABSTRACT

Bonding of polished, polycrystalline diamond films to silicon was performed in ultra high vacuum at 32 MPa of applied uniaxial stress. The transmission electron microscopy (TEM) investigation revealed that the interface of all bonded samples was non-uniform. An abrupt boundary between the two wafers existed only in some parts of the interface, while other parts contained an amorphous interlayer of up to 40 nm in thickness. Electron energy loss spectroscopy (EELS) revealed that this interlayer consisted of oxygen, carbon and silicon. Based on comparison of the microstructure and chemical composition of the interface formed at different bonding temperatures, we propose a model for the silicon/diamond wafer fusion process.

INTRODUCTION

Integration of diamond with other electronic materials is of considerable technological interest. Silicon-on-diamond (SOD) technology can significantly enhance power characteristics of devices fabricated on silicon, due in-part to the high thermal conductivity of diamond. Wafer bonding is a promising way to create these substrates, and generally involves an applied load and elevated temperature to promote a robust fusion. As such, the fusion interface must be scrutinized after this processing, since defects incurred are likely to influence the properties of the SOD substrates. This work reports on TEM studies of the bonded silicon/diamond interfaces formed in the temperature range between 950°C and 1100°C.

EXPERIMENTAL DETAILS

In all bonding experiments, we used commercially available CZ (001) Si wafers with a root-mean-square (RMS) surface roughness of ~0.5 nm and polycrystalline diamond films deposited using microwave plasma chemical vapor deposition, which were mechanically polished to an RMS roughness of ~15 nm. Possible graphitic contamination and polishing residues were removed from the diamond surface by cleaning the samples in a mixture of chromium oxide and sulfuric acid heated to 100°C. Prior to fusion, samples were ultrasonically cleaned in solvents and blow-dried in nitrogen. To limit particulate contamination, this procedure was performed inside a class 1000 clean-room. The final cleaning step was performed in ultra high vacuum (UHV), where diamond and Si samples were heated at 400-500°C for 2 hrs to desorb adventitious species such as carbon and oxygen. In addition, Si samples were heated at 1100°C for 60 min in order to remove the native oxide from the Si surface. An *in-situ* investigation of the surfaces using x-ray photoelectron spectroscopy (XPS), by obtaining both core level spectra and C 1s EELS data, verified removal of the surface contaminants. After the high temperature treatment, no change in the Si surface topography was observed by atomic force microscopy.

Wafer bonding was performed in a dedicated UHV chamber under a uniaxial stress of 32 MPa in the temperature range of 950°C to 1100°C. A bonding time of 15 hrs was chosen for all experiments. The details of this processing are described elsewhere [1]. The structural properties and chemical composition of the bonded interface were investigated using cross-sectional TEM (XTEM) and TEM EELS, respectively. Due to the challenge of thinning diamond bonded to silicon, XTEM samples were prepared using the focused ion beam technique. A 200 kV field-emission transmission electron microscope (JEOL 2010F) with an imaging filter (Gatan GIF) was used for the TEM analysis.

RESULTS AND DISCUSSION

Successful bonding of diamond films to Si was observed at temperatures as low as 950°C. Attempts to bond these samples at 850°C were unsuccessful.

Transmission Electron Microscopy

TEM images of the polycrystalline diamond fused to silicon at 950°C revealed that the interface between the two materials was not uniform. Silicon was in intimate contact with diamond only along some portions of the interface, as seen Fig. 1(a). Other parts of the interface contained an intermediate layer of up to 40 nm in thickness. A high-resolution image of Fig. 1(b) clearly shows that the layer is amorphous. Interestingly, the thickness of the interlayer was similar to the peak-to-valley roughness of the diamond films used in these experiments.

Fig. 2 shows a region containing an abrupt interface adjacent to an amorphous interlayer. Dislocations in silicon, seen in this micrograph, might be connected to instantaneous plastic deformation occurring near diamond surface asperities where stress was strongly concentrated, leading to values exceeding the Si yield stress of ~1 GPa. Alternatively, dislocations may be related to time dependent creep deformation which does not require such high stress values [2].

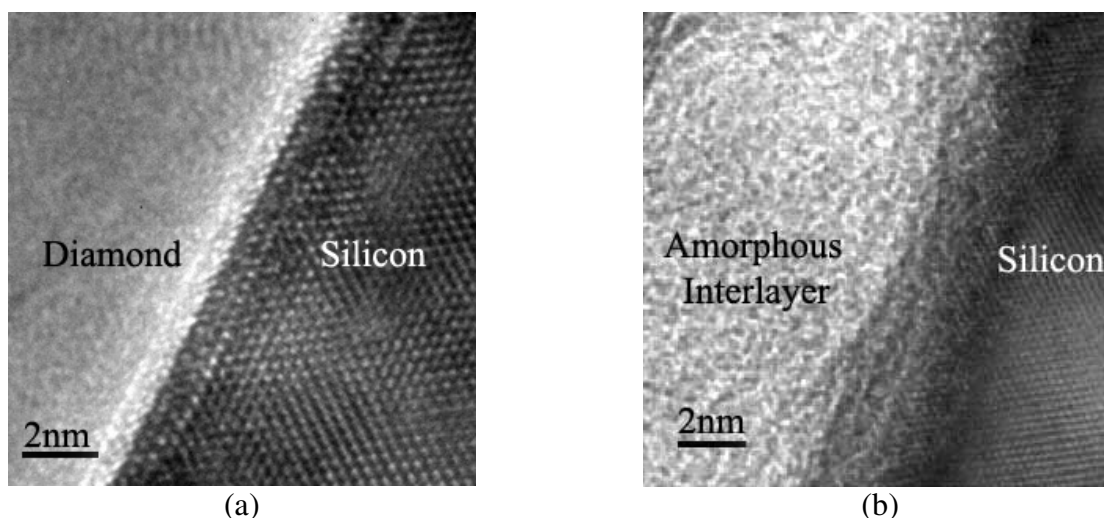


Figure 1. XTEM of the silicon/diamond interface fused at 950°C. High-resolution images show an abrupt boundary between Si and diamond observed in some parts of the interface (a) and an amorphous interlayer of up to 40 nm in thickness between the Si and diamond observed in other interface regions (b).

All dislocations found in the silicon were located in the abrupt interfacial regions close to the amorphous interlayer. No dislocations were seen elsewhere in silicon. In addition, no dislocations associated with the bonding process were observed in the diamond film, which is likely due to the high strength of diamond. Interestingly, in all areas observed by TEM the initially rough diamond (RMS roughness of 15 nm) was found to be almost atomically smooth following bonding. An amorphous phase periodically protruded into what had been initially a smooth silicon interface, as seen in Fig.2.

Several observations made during various stages of the fusion process suggest that unintentional surface contamination prior to bonding was not responsible for the formation of this amorphous phase. First, an analogous study involving bonding of Si to SiC, using the same procedure, did not result in the formation of a similar interfacial layer. Secondly, XPS revealed a carbon concentration of less than one percent on the cleaned Si surface, while XPS carbon EELS revealed only a sp^3 -bonded carbon component in the near surface region of the cleaned diamond. Finally, optical microscopy of the wet-cleaned wafers showed very little evidence of particulate contamination on these surfaces prior to bonding, which discounts the possibility that the interlayer was formed from particles originally residing on the wafer surfaces.

To investigate the origin and temperature dependence of the amorphous interlayer, an XTEM study of a second sample bonded at higher temperature (1150°C) was performed. If the thickness of the interlayer were determined only by the kinetics of the process, then considerably thicker interlayer regions would be expected with temperature. The TEM images, however, revealed an interface nearly identical to that obtained at 950°C. The maximum thickness of this interlayer was again on the order of 40 nm, and a mixture of abrupt and amorphous interlayer regions were observed, although the relative area of intimate contact between the diamond and the silicon appeared to be smaller. Again, the diamond surface was very smooth across the entire region. Interestingly, no dislocations were observed in the silicon portion of this interface region, presumably because of greater dislocation mobilities at the higher fusion temperature leading to their being annealed out.

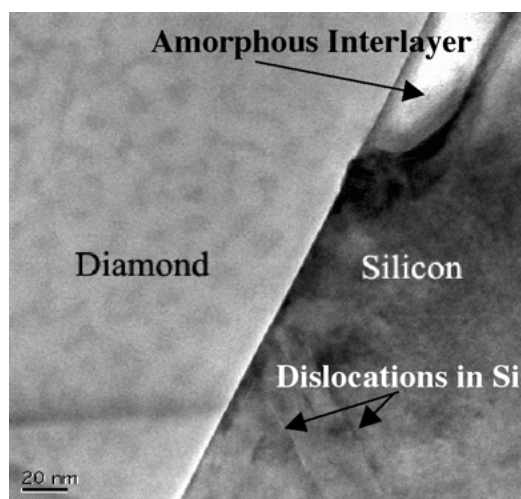


Figure 2. XTEM of the silicon/diamond interface fused at 950°C. An abrupt interface adjacent to an amorphous interlayer. Dislocations propagating into the Si are evident in this region. Amorphous material occupied regions within silicon creating wells in initially smooth silicon wafer.

Electron Energy Loss Spectroscopy

To investigate the composition of the amorphous layer observed in the silicon/diamond bonding interface, EELS was performed in the scanning mode of the transmission electron microscope. This afforded precise control over the area where the spectra were taken. EELS spectra of the amorphous interlayer showed the presence of oxygen, silicon, and carbon. A typical composition profile across this interlayer for the sample bonded at 950°C is presented in Fig. 3(a). Close to the silicon wafer, the interlayer was comprised mainly of silicon. The silicon concentration monotonically decreased while the carbon concentration increased as one crossed towards the diamond layer until the interlayer was solely amorphous carbon. It is evident that significant inter-mixing of carbon and silicon took place within the interlayer during the bonding process.

Although the adventitious oxygen was removed from the surface of the Si wafer prior to bonding, there were significant amounts of oxygen (~40 at. %) detected within the amorphous interlayer, as can be seen in Fig. 3(a). One likely source of the oxygen is from the CVD diamond. Although the level of oxygen impurities in these diamond films is not known, it very likely exceeds the equilibrium solid solubility limit for diamond at the fusion temperatures. The polycrystalline nature of the diamond samples would have certainly permitted accelerated diffusion along the grain boundaries. So, it seems quite plausible that oxygen diffusion out of the diamond film could have accounted for the high concentrations of oxygen found in the amorphous phase. A similar out-diffusion of supersaturated oxygen from the silicon wafer towards the interface has been observed in some silicon-to-silicon bonding experiments [3], but it is not believed to have been a primary contributor here. Assuming that the interlayer covered fifty percent of interface and that the oxygen concentration in our Si wafers was $2.5 \times 10^{18} \text{ cm}^{-3}$, one can calculate that the oxygen concentration in the interlayer should not have exceeded 3%. Finally, the authors cannot rule out the possibility that part of the observed oxygen may have been introduced during TEM sample preparation leading to greatly exaggerated values. Nonetheless, the amorphous nature of the interfacial layer does appear to be connected to the observed high concentration of oxygen. Kanenko *et al.* [4] studied the structure and the chemical bonding of Si-O-C ceramics and found that at higher oxygen contents it tended to form an amorphous microstructure.

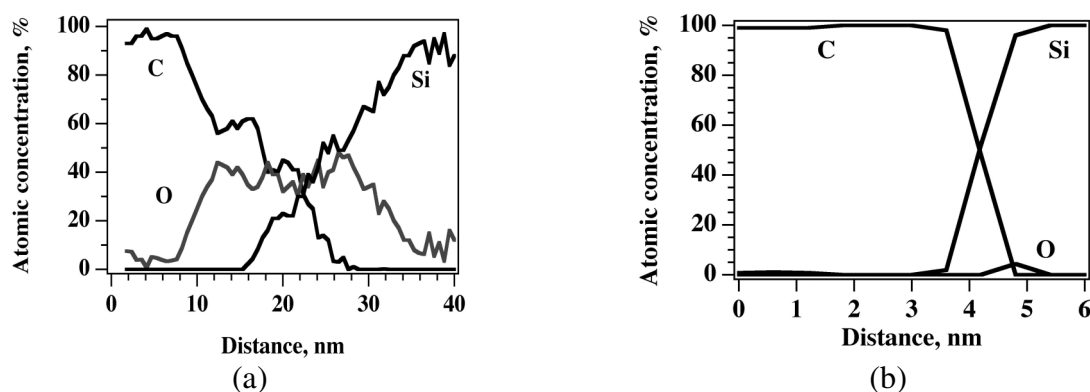


Figure 3. Composition change across the intermediate amorphous layer (a) and the abrupt silicon/diamond interface (b) fused at 950°C.

A series of EELS spectra were taken also across the abrupt silicon/diamond boundary (see Fig. 3(b)). No silicon was observed in the diamond film and no carbon was found to be present in the silicon wafer. This behavior is markedly different from that previously described where significant intermixing of the silicon and carbon was observed within the interfacial layer (see Fig. 3(a)). This phenomenon can be explained by phase transformation of diamond to graphite due to a high localized pressure as a result of the non-planarity of the diamond surface.

Model of the silicon/diamond bonding process

Under ambient pressure conditions, diamond is an unstable form of carbon and will eventually transform into graphite. However, the graphitization rate is greatly affected by various factors including temperature, gaseous ambient, applied pressure, defect content, and crystallographic orientation [5] making simple predictions difficult. For example, S. Kumar *et al.* reported on diamond surface stability in a hydrogen atmosphere (760 Torr) at temperatures up to $\sim 2200^\circ\text{C}$ [6]. At the same time, Evans and Phaal [7] have found that the $\{100\}$ and $\{111\}$ faces of diamond start to graphitize in the presence of oxygen ($6 \cdot 10^{-2}$ Torr) at considerably lower temperatures of 850°C and 700°C , respectively. In other work, Gogotsi *et al.* [8] observed the transformation of diamond to disordered graphite during indentation tests performed at room temperature in air where nominal compressive stresses approached 100 GPa. This finding appears to contradict the well-known fact that graphite transforms into diamond at high pressures. However, Gogotsi's study was performed under uniaxial (not hydrostatic) loading conditions and conducted in the absence of a catalyst. Contact loading not only compresses the diamond bonds but it also changes the bond angle and this apparently promotes the transformation of diamond to graphite.

Prior high temperature work [5-11] indicates that surface oxide and applied mechanical load should facilitate graphitization. It is also known that surface graphitization is an autocatalytic process which starts at discrete sites and then spreads out. Thus, it seems very plausible in the present bonding studies that graphitization initiates at diamond surface asperities, since these are high stress concentration areas. Following initial graphitization, the carbon atoms may interact with the silicon wafer and any free oxygen to form regions of amorphous material. This process will continue until the diamond surface roughness is completely accommodated by local plastic deformation of silicon and interdiffusion of silicon and carbon.

The diamond-to-graphite transformation is accompanied by an increase in volume. This leads one to conclude that graphitization of the diamond surface should decrease as a continuous bonded interface is approached. A fusion interface comprised of open gaps could accommodate this volume change through lateral expansion into these voids. However, this is no longer possible once a continuous bonded interface develops. At that point the needed volume increase can only be provided by working against the applied load. This should increase the activation barrier for the transformation and considerably slow down its rate. Concurrently, the stress is also diminishing as the contact area increases. These effects may combine to significantly slow down the phase transformation rate as the bonding process proceeds to completion.

It is also known that the formation of a step height equal to or greater than one atomic layer facilitates graphitization [11]. Once a step is formed, fewer C-C bonds per atom need to be broken for this transformation to progress. Thus, lateral propagation of the graphitized diamond from surface steps might explain the smooth diamond interface that was observed in the present bonding studies. Differences in the oxidation and graphitization rates along the various crystallographic directions might also play some role in the observed phenomenon.

It is well accepted that carbon atoms strongly enhance oxygen precipitation in silicon, and for the case of co-precipitation of oxygen and carbon in silicon, it is common to find both

constituents in the same precipitate [12-14]. Presumably, carbon atoms released from diamond following graphitization acted as gettering sites for oxygen precipitation within the bonded interface. Discriminate carbon and oxide clusters would lead to an increase in the total system energy of the interface [14], which may explain the more energetically favorable formation of a Si-O-C amorphous interlayer.

SUMMARY

Bonding of polished, polycrystalline diamond films to silicon performed in ultra high vacuum at 32 MPa of applied uniaxial stress resulted in the formation of a non-uniform interface. An abrupt boundary between the two wafers existed only in some parts of the interface, while other parts contained an amorphous interlayer of up to 40 nm in thickness consisting of carbon, silicon and oxygen. Local phase transformation of diamond to graphite near the diamond surface asperities, followed by interdiffusion of C and Si, is the most likely mechanism leading to formation of this amorphous interfacial layer.

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