Si$^+$ implantation: A pretreatment method for diamond nucleation on a Si wafer

Jie Yang$^{a,b)}$

The State Key Laboratory of Surface Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People’s Republic of China and a member of CCAST (World Laboratory)

Xiaowei Su

National Laboratory for Materials Modification by Laser, Ion and Electron Beams, Dalian University of Technology, Dalian 116023, People’s Republic of China

Qijn Chen and Zhangda Lin$^{b)}$

The State Key Laboratory of Surface Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People’s Republic of China

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Diamond films have been obtained by the hot-filament chemical vapor deposition method on a silicon wafer. The substrates were preimplanted by a Si$^+$ ion beam (ion energy 25 keV, implantation dosage $2\times10^{17}$ Si/cm$^2$).

$^a$Author to whom correspondence should be addressed.

$^b$Electronic mail: zdlin@bepc2.ihep.ac.cn

The nucleation of diamond is an essential step for the diamond film synthesis, which depends on the substrate material and is greatly affected by the initial surface conditions of the substrate. From a technological point of view, silicon, as the basic material for present microelectronics, is strongly favored as a substrate material for thin film diamond devices. Diamond growth on Si has received more attention than diamond growth on other materials. However, the high lattice mismatch and high surface energy difference between silicon and diamond [the lattice parameter of Si is $a=0.543$ nm and the surface energy of the Si(111) plane is 1.5 J m$^{-2}$, while the lattice parameter of diamond is $a=0.356$ nm and the surface energy of diamond is 6 J m$^{-2}$ (Refs. 3 and 4)] have caused considerable controversy about possible diamond growth on silicon substrates. In general, owing to the high surface energy of diamond and the relatively low sticking probability of the precursor for diamond nucleation, diamond nuclei grow very poorly on a mirror-polished silicon substrate. Therefore, pretreatment of the substrate is commonly applied to obtain diamond films on Si wafers. The nucleation density can be enhanced by (1) scratching or abrading the surface of the substrate with diamond,$^6$ SiC,$^7$ and cubic BN,$^8$ as well as stainless steel$^9$ grit paste; (2) creating submicrometer-scale craters by 25 keV Ga$^+$ focused ion beams;$^{10}$ (3) sputtering with 0.5 keV Ar$^+$; (4) preferentially etching in a solution of KOH to create micrometer-scale V grooves; (5) coating with a low vapor pressure and high thermal stability hydrocarbon oil;$^{11}$ (6) coating with a thin layer of evaporated carbon;$^{12}$ and (7) applying a substrate bias voltage,$^{13,15}$ etc. Because the growth mechanism of the diamond film is complex, it seems that a growth model derived from a specific condition may not be generally applicable. In the above pretreatment methods, many factors affect the nucleation of diamond; for example, residual diamond seeds, carbon precursor, the change of surface stress, and formation of carbide, etc. It is not easy to distinguish these different factors from the above pretreatment methods. In this letter, Si$^+$ ion beam implantation was used to pretreat the silicon wafer. It is believed that surface stress predominates diamond nucleation. Experimental results show that diamond can nucleate and grow on these preimplanted Si substrates from the vapor phase under low pressure by chemical vapor deposition (CVD). Because the ion implantation technique is very reliable, the parameters of energy and dosage can be controlled conveniently, and thus this method has significance not only in theory but also in application.

Mirror-polished n-type silicon (100) wafers were used as substrates. Si$^+$ ion implantation was carried out at $E=25$ keV in a MEVVA IV80-10 ion implantation system (made in the USA). The ion current density was about 30 $\mu$A/cm$^2$. The implantation dosage of $2\times10^{17}$ Si/cm$^2$ was controlled by ion current density and implantation time. The sample had been cleaned with a typical chemical cleaning process, which included washing by a cleaning solution, etching in dilute hydrofluoric acid for 20 s, cleaning with acetone, and washing with de-ionized water before loading. The vacuum during the implantation was maintained at better than $3\times10^{-4}$ Pa. The samples were not specially heated. After implantation, the samples were taken out and cleaved into $2\times1\text{ cm}^2$ oblongs. The diamond film was deposited on a Si substrate in another system, a typical hot filament chemical vapor depo-
sition (HF-CVD) device that is similar to that of Chu et al.\textsuperscript{16} A φ140 and 500 mm long quartz tube was used as the deposition chamber. A copper platform 80 mm in diameter was used to support the samples. φ0.2 mm tungsten wires coiled 2.5 mm in diameter were used as filaments, with their temperature measured by an optical pyrometer. The source gas was diluted CH\textsubscript{4} in hydrogen at a ratio of 0.8\% with a total flow rate of 100 sccm (standard cubic centimeter per minute). The distance between the filament and the substrates was fixed at 5 mm. Filament temperature was 2100 °C; substrate temperature was held at 830 °C, as measured by a thermocouple (PtRh); growth time was 24 h.

X-ray diffraction (XRD) analyses were completed on the x-ray diffractor (D/max-RB, 12 kW, Cu Ka) to characterize the structure of synthesized film. Scanning electron microscopy (SEM) (the type is S-450) was used to study the surface and cross-sectional morphology of the films. The quality of the synthesized films was characterized by Raman spectroscopy (SPEX 1403, 400 mW, Ar\textsuperscript{+} laser, wavelength 514.5 nm).

As indicated by SEM photographs shown in Figs. 1(a) and 1(b), it is clear that well-distributed and continuous polycrystalline diamond film with good crystalline facets has been synthesized and total thickness of the diamond film is about 12 μm.

Figure 2 is a Raman spectrum of the as-grown diamond film with 488.0 nm Ar\textsuperscript{+} ion laser excitation. The sharp and strong diamond peak appears at 1332 cm\textsuperscript{-1}, and the graphite peak near 1580 cm\textsuperscript{-1} is very low. It shows that the synthesized diamond film is of good crystallinity.

Figure 3 shows the XRD diagram of synthesized film on a Si(100) wafer. Si(400), diamond(111), (220), (311), and (400) diffraction peaks are observed. Diamond diffraction peaks are sharper than the Si diffraction peaks. This diagram indicates that polycrystalline diamond film with high quality crystals had been synthesized.

The character of surface implantation was taken into account in the choice of the implantation energy. Because the peak of ion distribution is in the subsurface of the substrate and the distance between this peak and substrate surface increases with the increase of the implantation energy, lower energy ion implantation can result in changing the surface stress while keeping the bulk Si wafer’s properties. The implantation energy affects not only the ion R\textsubscript{p}, but also the ion distribution in substrates. In our experiment, accordingly, the implantation energy was fixed at 25 keV, which is the lowest available energy for Si\textsuperscript{+} implantation in our ion implantation system. Monte Carlo calculation (performed by TRIM-94 computer program\textsuperscript{17}) shows Si\textsuperscript{+} and ionization distribution in the Si substrate at an implantation energy of 25 keV. The calculated ion longitudinal range (R\textsubscript{p}) is about 40 nm and straggle (ΔR\textsubscript{p}) is about 17 nm. Experiments with other different implantation dosages (5×10\textsuperscript{13}, 1×10\textsuperscript{16}, and 5×10\textsuperscript{15}) have also been performed. As the implantation dosage increases, the diamond nucleation density increases. To find the best combination of the parameters (energy, dosage, and temperature, etc.), more detailed and systematic experiments are needed. The detailed results and discussions of Monte Carlo calculation and experiment with different implantation dosages will be published in another paper.\textsuperscript{18}

Ion implantation can increase the surface energy of the Si substrate because it involves the process of atomic displacements. This process results from collisional events, radiation-enhanced diffusion, and thermal spikes to different degrees, depending on the crystal structure layer and substrate substance.\textsuperscript{19,20} Ion implantation can reduce the difference of surface energy between the Si wafer and the diamond film and enhances the nucleation of diamond on substrate.

Based on previous work,\textsuperscript{10-14} nanoscale microstructures are effective nucleation sites for diamond growth. Ion beam implantation can change the surface structure of the Si wafer on the nanoscale level. Two possible factors are related to the changes of surface morphology to affect the diamond nucleation. First, ion implantation favors the formation of precursors of diamond, for example, SiC and amorphous carbon, etc; second, it increases the sticking probability of these diamond precursors on the Si wafer. However, compared with
mechanical scratch and chemical etch methods, Si⁺ implantation has less effect on the surface morphology of the Si wafer. It causes no visible surface damage or roughness viewed with an optical microscopy, while the others usually make the sample surface rougher. XRD results show that no SiC has been found. For comparison, a mirror-polished Si wafer without implantation has also been used as substrate under the same nucleation and growth conditions. However, no diamond film has been deposited on them. Therefore, we believe that the change of the surface stress of the Si wafer is the dominant factor for diamond nucleation and growth on the Si wafer in our experiments. A very important advantage of this pretreatment method is that it is compatible with other pretreatment methods. It can be used as a first step in combined pretreatment methods.

In summary, Si⁺ implantation, a new method having no surface mechanical damage of the substrate for enhancing diamond nucleation on a mirror-polished silicon wafer, has been achieved. Well-distributed and continuous polycrystalline diamond film with high quality crystals has been synthesized by the hot-filament chemical vapor deposition method. The surface stress is believed to be one of the most important factors for low pressure diamond nucleation on the Si wafer.

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