Surface passivation in diamond nucleation

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Surface passivation is introduced to suppress the deleterious effect of Si surface oxides and thus enhance diamond heteroepitaxial nucleation. Surface composition and diamond nucleation and growth on H-, Br-, and I-passivated Si surfaces were studied. X-ray photoelectron spectroscopy showed that the passivated Si surfaces were free of silicon oxides and carbides. Remarkable enhancement in nucleation was achieved on passivated surfaces and the nucleation density obtained on a Br-passivated Si surface reached $10^{10}\,cm^{-2}$. Programmable temperature desorption revealed that the adsorbate desorption temperature increased in the order of H, I, and Br passivation. The same order of increase was also observed in the saturation value of electron emission current from the passivated surfaces, which was related to the degree of nucleation. Nucleation enhancement was shown to be greater when the adsorbate desorption temperature is closer to the nucleation temperature, so that more adsorbate- and oxide-free Si surface area would be available for nucleation. The study established that surface passivation is potentially an effective approach for diamond heteroepitaxial nucleation.

INTRODUCTION

Large-area epitaxial single crystalline diamond film has long been expected since the highly oriented polycrystalline diamond films were grown heteroepitaxially on Si by Jiang *et al.*[1] Despite the intensive effort devoted to the epitaxial growth of diamond film on Si, little progress has been made since the early success.[1] One of the reasons that epitaxial single crystalline diamond films cannot be achieved is possibly due to the fact that the Si surface is very reactive and a thin oxide layer (SiO or SiO_2) forms easily on the surface. Even when starting with a clean Si surface, the trace amount of oxygen and water vapor in the growth chamber may induce the formation of oxide layer, which inhibits the epitaxial growth and may eventually suppress diamond deposition. As such, it is unlikely that a single crystalline diamond film can be deposited on a partially oxidized Si surface.

The scanning Auger microscopy results of Tanaka *et al.*[2] showed that diamond nuclei were competitively deposited with silicon oxide on the Si surface. Therefore, removal of oxide on the Si surface may effectively enhance diamond growth, as pointed out by Bergmaier *et al.*[3] Because diamond nucleation and growth by chemical vapor deposition (CVD) were achieved in an H_2 environment, a small amount of oxygen would normally be acceptable in diamond growth. However, Schreck *et al.*[4] found that the introduction of 75 ppm of CO_2 (corresponding to a C:O ratio of 600:1) into the gas mixture would seriously suppress the nucleation and growth area of diamond. Kang *et al.*[5] also revealed that increasing oxygen contamination in the reactant gases greatly reduced the diamond nucleation density on Si. Thermodynamically, a hydrogen/oxygen ratio greater than 10^6 would be necessary to reduce CO_2 thermally at 1 bar and at a temperature typical for diamond CVD growth, i.e., 800–900 °C.[3]

Generally, the H_2 source contains a very small amount of O_2 and H_2O, while the base pressure of a CVD chamber is typically larger than 10^{-7} torr. As a result, the trace amount of O_2 and H_2O present in the H_2 and CH_4 sources and/or the residual ambient during CVD growth not only compensates the reduction process by the activated hydrogen but further leads to new oxidation of the Si surface.

The oxide layer can be partially removed by positive ion bombardment on the Si substrate through the applied negative bias voltage, as suggested by Yugo *et al.*[6] However, diamond heteroepitaxy would be difficult due to the damage of lattice structure caused by ion bombardment. Thus, the positive and negative effects of ion bombardment coexist simultaneously. To compromise between the positive and negative effects of bias, the time for ion bombardment at a certain energy has to be limited in a certain range (time window).[7] Furthermore, it is difficult to remove the oxide layer completely with unlimited ion bombardment. The partial removal of the oxide layer thus restricts heteroepitaxial growth to local regions.

In order to grow large-area diamond epitaxy, the surface oxide must be removed completely from the Si wafer before and during the nucleation and growth process. Or the oxygen effect at least should be minimized to a negligible level. To eliminate the oxygen effect, surface cleaning, and passivation of the Si substrate, purification of the hydrogen source and improvement of the chamber vacuum level are all useful and essential. This work represents an investigation of the effect of Si surface passivation on diamond nucleation and growth.

EXPERIMENTAL DETAILS

Diamond nucleation and growth were performed in a microwave plasma chemical vapor deposition (MP-CVD) system (from ASTEX™). The base pressure in the deposition chamber was 5×10^{-7} torr. The substrates were placed on a graphitic substrate holder, which was inductively heated. The temperature of the substrate holder, measured by the thermocouple, was used to control the power of the induction heater. The substrates were mirror-polished *p*-type (111) Si wafers, 3-in. in diameter and with a resistivity of 7 Ω cm.

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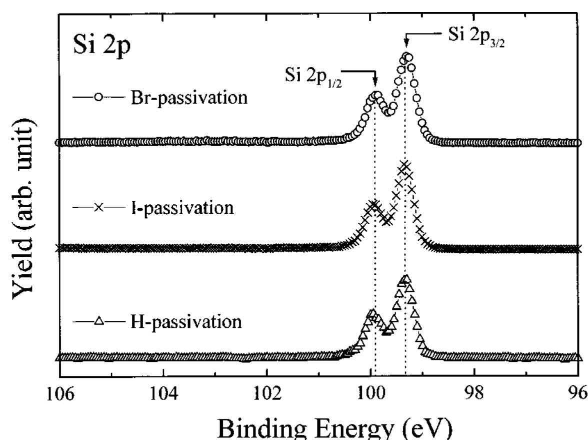

FIG. 1. XPS Si $2p$ core-level spectra taken from H-, Br-, and I-passivated Si, respectively.

The substrate was cleaned ultrasonically in acetone, ethanol, and deionized water for 10 min, respectively, then immersed in 20% HF solution for 2 min to remove the native oxide. The wafer was then treated with a H_2O_2:HCl:H_2O (in a volume ratio of 3:1:1) solution for 5 min for reoxidation and immersed in a HF:NH_4E (1:3) solution for 8 min to remove oxide. Finally, the Si wafer was rinsed with deionized water. The above cleaning procedure gives Si substrates with H passivation.[8] By spraying the H-passivated Si substrate with Br methanol or I methanol under dry N_2 atmosphere, Br-passivated and I-passivated Si substrates were obtained, respectively.[9]

The nucleation density and surface morphology of diamond were characterized by scanning electron microscopy (SEM, PHILIPS XL-30 FEG). Meanwhile, to evaluate the diamond nucleation density over the whole substrate area, we monitored the time dependence of the biasing current to determine the nucleation behavior and total area of diamond nuclei of the passivated Si substrates, as suggested by Schreck *et al.*[4,10] To characterize the as-grown products, we used Raman spectroscopy (taken by Renishaw Raman System 2000), with a spectral resolution of 1 cm^{-1} and a spatial resolution of 1 μm. For checking surface cleanliness, XPS (VG ESCALAB 220i-XL) with a Mg $K\alpha$ x-ray source was used. The pass energy was kept at 20 eV giving an energy resolution of 0.5 eV.

RESULTS AND DISCUSSION

A. Surface cleanliness of Si under different surface treatment

Figure 1 shows the XPS spectra of H-, Br-, and I-passivated Si surfaces. No SiO_x or SiC peaks were detected, while only the Si $2p_{1/2}$ and Si $2p_{3/2}$ peak components appeared in the spectra. This indicates that the Si surface was free of oxides and carbides. Therefore, it can be concluded that by using the surface passivation method we were able to obtain a fairly clean surface of Si. In the survey XPS spectrum, however, a small amount of oxygen and carbon was found in addition to Si, Br, or I. Although oxygen and carbon were detected after chemical cleaning, the trace amount of oxygen and carbon was probably physically adsorbed rather than directly bonded to the surfaces of the H-, Br-, and I-passivated Si substrate as no Si oxide and carbide peaks were detected in the Si $2p$ spectrum. To remove the adsorbed oxygen and carbon traces, a low-temperature pretreatment[11,12] was carried out before diamond nucleation. The process was achieved in the MP-CVD chamber by using a 1% CH_4/H_2 gas mixture, a microwave power of 600 W, and a substrate temperature of 220 °C for 30 min.

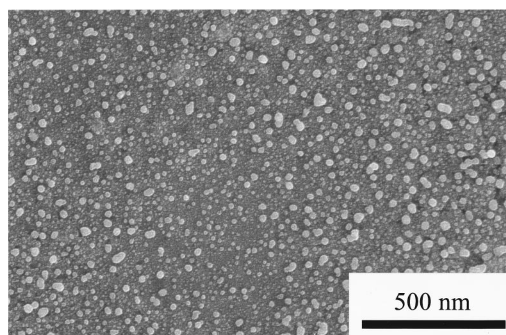

FIG. 2. Diamond nucleation density on Br-passivated Si substrate. Temperature, 620 °C; nucleation time, 30 min, $CH_4/H_2 = 1\%$; microwave power, 1000 W.

B. Effect of Si surface passivation on diamond nucleation

Figure 2 shows the SEM picture of the nuclei density on a Br-passivated Si substrate. After removal of surface oxygen and carbon as mentioned above, the substrate temperature was increased to 620 °C for nucleation and the time was kept at 30 min. The gas mixture used was $CH_4/H_2 = 1\%$ and the microwave power was 1000 W. From Fig. 2, the nucleation density was measured to be $6\times10^{10}\,cm^{-2}$, which is comparable to the highest nucleation density level of $5\times10^{10}\,cm^{-2}$ obtained under 200 V negative bias treatment reported by Stoner *et al.*[11] The grown surface species was characterized by Raman spectroscopy. Besides the characteristic diamond peak at 1332 cm^{-1}, the graphite peak at 1580 cm^{-1} is also present in Fig. 3(a). After a continuous growth of 5 h at 620 °C, the sharp diamond peak became dominant in the spectrum and the graphite peak was hardly detectable [Fig. 3(b)]. The morphology of the as-grown diamond is shown in Fig. 4, which shows the typical polycrystalline CVD diamond film. It is important to point out that extremely high nucleation density was obtained without applying a bias voltage to the Si substrate and at a comparatively low temperature of 620 °C. Why can such a high nucleation density be achieved on Br-passivated Si substrate? We believe that the main reason lies in the fact that Br was able to effectively prevent the Si surface from oxidation until it de-

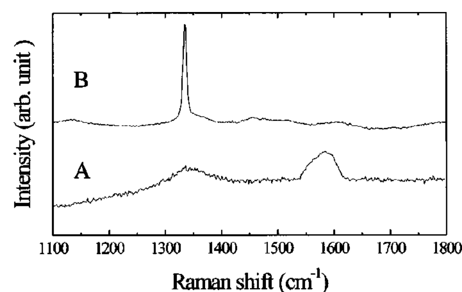

FIG. 3. Raman spectra of diamond nucleation (A) and growth (B) on Br-passivated Si.

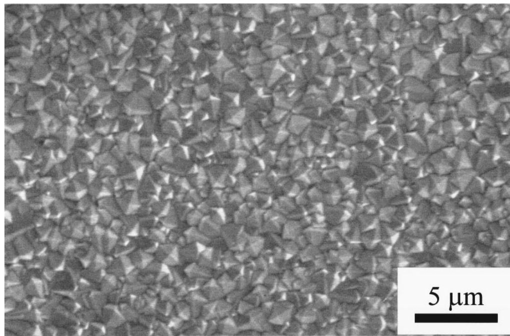

FIG. 4. SEM of Fig. 3 (*B*) sample after growing for 5 h.

sorbed from the surface. The desorption temperature of Br was comparatively high at 578 °C (shown in Fig. 5), as measured by a temperature programmable quadrupole mass spectrometer. As a result, Br species would only start to desorb when the Si substrate temperature was close to 620 °C, where diamond nucleation would initiate. The time elapse between Br desorption and diamond nucleation was very short, thus minimizing the oxidation probability of Si. Since diamond would easily nucleate on the fresh Si surface free of oxygen, the resulting diamond nucleation density would be high. If the Si surface were H-passivated, the situation would be quite different. Since the desorption temperature of H on the Si surface was 258 °C (shown in Fig. 5), hydrogen would have been completely desorbed as the temperature ramped up to 620 °C from 258 °C. The time elapse between H desorption and diamond nucleation would be comparatively longer than that for the Br-passivated Si surface. Since a small amount of O_2 and water vapor was inevitably present in the growth chamber (with a base pressure at 5×10^{-7} torr and the gas reagent used), oxidation would be

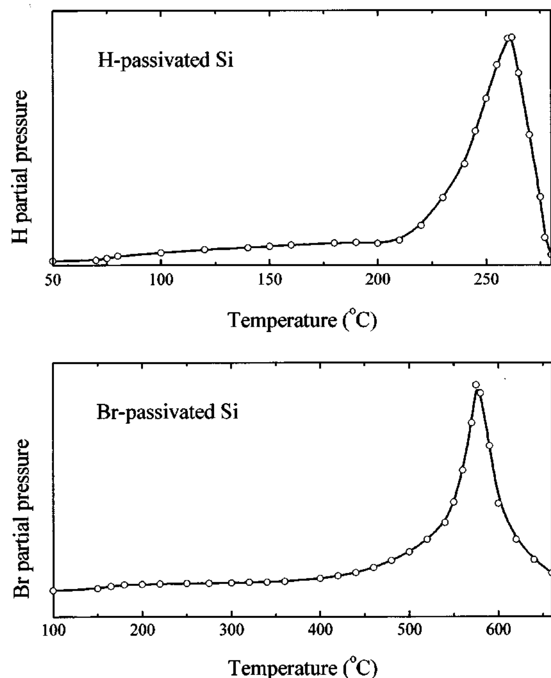

FIG. 5. Temperature programming desorption curves for H and Br on Si(111); measured by QMS. Temperature rises in a rate of 2.5 °C/min.

appreciable for a H-passivated Si surface at the nucleation temperature. As the surface oxide would obstruct diamond nucleation, diamond nucleation density would thus be comparatively low, generally in the range of 10^6-10^8 cm^{-2}.

The oxygen effect also plays a role in other nucleation enhancement. Recently, Kang *et al.*[5] reported that under the condition of 10^{-10} torr base pressure and high-purity H_2 gas, a diamond nucleation density of 10^{10} cm^{-2} was obtained on a mirror-polished Si surface with no negative bias. However, if 0.16% O_2 were added to the gas mixture, the nucleation density would drop to 10^7 cm^{-2}. In the bias-enhanced nucleation method,[1,6,11] positive ion bombardment can partially remove the oxide layer on the Si surface. Since diamond can nucleate readily on oxide-free Si surfaces, nucleation density may thus increase to $10^{10}-10^{11}$ cm^{-2}. On the other hand, ion bombardment-induced damage and partial surface oxide removal disrupt the periodicity of the surface lattice structure, therefore epitaxial nucleation is eventually difficult over a large area.[13,14]

To further elucidate the effect of surface passivation, diamond nucleation on the I-passivated Si surface was also studied. No prominent enhancement effect was found for nucleation on I-passivated Si at 620 °C. This can be explained by the fact that the desorption temperature of I was much lower than that of Br but higher than that of H. Although we could not measure the desorption temperature of I (the mass of I is beyond the measurement range of our QMS), we estimated it from the binding energy of the Si-I and Si-Br bonds (293 and 367.8 kJ/mol, respectively[15]) to be around 460 °C. Consequently, as the substrate temperature ramped up to 620 °C, iodine would have been completely desorbed from the Si surface and the Si surface exposed to oxidation by the CVD ambient well before nucleation started at 620 °C. Therefore, the diamond nucleation density on I-passivated Si was intermediate between those on H-passivated and Br-passivated Si surfaces.

C. Comparison of substrate biasing current with different Si surface passivation

Since the electron emission from a diamond surface is much stronger than from a bare Si surface, an increase in current under negative substrate bias during the nucleation process can be correlated to the diamond coverage on a Si wafer, as discussed by Schreck *et al.*[4,7] Therefore, the temporal evolution of bias-induced substrate current provides an insight into the diamond nucleation behavior while the saturation value of biasing current gives an estimate of the relative diamond coverage on Si. The experimental details are as follows. The passivated Si substrate was kept at 510 °C, slightly lower than the desorption temperature of Br, and applied with a 180-V negative bias under a 3%, CH_4/H_2 gas ambient and a microwave power of 1200 W. Figure 6 depicts the time dependence of the biasing current from the passivated Si surfaces. Comparison of the three curves shows two distinct features. First, the bias current increased rapidly to a saturation value after 240 min for the H-passivated sample. For the Br-passivated sample, the change in bias current versus nucleation time was relatively slow compared to the H-passivated sample. It took approximately seven hours to reach its saturation value. The rate of increase in bias current

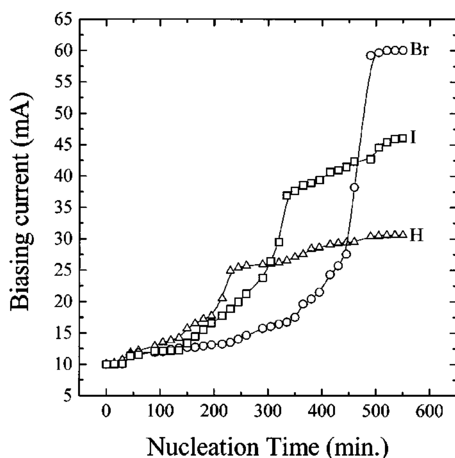

FIG. 6. Temporal evolution curves of induced biasing current for Si substrates passivated by bromine (Br), passivated by iodine (I), and passivated by hydrogen (H) during diamond nucleation.

for the I-passivated sample was less than that of the Br- and H-passivated samples. Second, the value of the saturation bias current was in the order of H passivation less than I passivation less than Br passivation, with the Br-passivated sample having the highest saturation bias current. This indicates that the Br-passivated Si substrate had the largest coverage of diamond nuclei among the three.[4,7]

The two prominent features stated above are consistent with the nucleation behavior of the three passivated Si substrates. Owing to the ease of H desorption at temperatures below 510 °C, the Si substrate would be exposed first and nucleation would start earliest on the H-passivated Si, as evidenced by a rapid increase in bias current. This is consistent with the results reported by Schreck *et al.*[4,7] For the Br-passivated sample, since the substrate temperature (510 °C) was slightly (68 °C) lower than the Br desorption temperature (578 °C), Br desorption would be slow, although it could be assisted by ion bombardment. As a result, the Si surface would be exposed very slowly and diamond nucleation would begin very late, as evidenced by the slow increase of biasing current at 7 h (Fig. 6). The explanation for the trend of the saturation bias current follows similarly. At 510 °C, H desorption has long completed; the probability of Si substrate exposure to oxygen in the chamber is high. Consequently, the nucleation process will soon be blocked and the area covered by nuclei is small. For the Br-passivated Si surface, Br desorption was primarily induced by cation bombardment. Moreover, during the bombardment, diamond was formed simultaneously. Therefore, the probability of the bare Si surface being exposed to oxygen would be very low. As a result, an increase in nucleation area and thus the largest saturation bias current were observed. These results are in good agreement with the SEM pictures of nucleated Si.

CONCLUSIONS

One difficulty for diamond epitaxial nucleation on Si was the competition between diamond nucleation and surface oxidation on Si. By minimizing surface oxidation during the nucleation process, surface passivation of Si has been shown to be an effective method for nucleation enhancement. We compared the effect of H, I, and Br passivation on diamond nucleation and concluded that Br passivation gave rise to the highest nucleation enhancement. Nucleation density on Br-passivation Si reached a level of $10^{10}\,cm^2$, which is comparable to the highest value obtained thus far by the bias-enhanced nucleation method.

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