Pinhole defects in MPCVD diamond films

Dongping Zhang (张东平), Jianda Shao (邵建达), Hongji Qi (齐红基),
Dawei Zhang (张大伟), and Zhengxiu Fan (范正修)

Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800

Received August 20, 2003

Diamond films were deposited in microwave plasma chemical vapor deposition (MPCVD) method on plain silicon substrates with (100) orientation. And the pinhole defects on them were investigated by optical microscopy and scanning electron microscopy (SEM). X-ray masks were fabricated with the films deposited by us. We found the pinhole defects in the film destroyed the gold absorber. The corrosion-resistance tests conducted in 30% KOH solution under 80 °C showed that the diamond films with pinhole defects have lower corrosion-resistance. In addition, the possible mechanism of the formation of pinhole defects in diamond films was discussed. And we deduced that the defects on substrates, competitive growth of multi-phase in diamond films, lattice dislocation between substrates and diamond films could be associated with the defect formation.

OCIS codes: 160.4890, 310.6870, 310.3840.

With the development of microelectronic technology, new materials may be necessary to develop X-ray masks that can meet with the requirement of the ultra-deep submicron (UDSM) level line width for ultra-large scale integration (ULSI) technique. Diamond is one of the materials that have many outstanding physical and chemical properties including low coefficient of expansion, high thermal conductivity, high transparency from far infrared to UV, high X-ray transparency, high stability for radioactivity, and etc.. These properties meet with the requirement of the X-ray lithography mask substrate materials[1]. A process of growing diamond films for X-ray lithography by chemical vapor deposition (CVD) method is a rapidly advancing technology at present. However, the defect of the pinholes is one of the main factors that influence the films' probability and stability of this application, and there are rarely reports mentioned about it. So it is necessary to make known about these. We will discuss these in details.

The films were prepared by microwave plasma chemical vapor deposition (MPCVD) technique. A mixture of 0.25% CH_4 in H_2 was used as a precursor gas to grow the diamond films. The substrates used in this study were n-type silicon wafers (10×10 mm^2) with (100) orientation, whose thickness is 0.5 mm. Before deposition the substrates were ultrasonic cleaned with de-ionized (DI) water. In this MPCVD system, the microwave power was about 1100 W, the frequency was 2.45 GHz, and the total pressure was about 35 torr. The deposition time was 3 hours, and the temperature of substrate was about 800 °C. These prepared samples were observed under the scanning electron microscopy (SEM) and optical microscopy respectively. The Raman spectra of the diamond films were recorded using the SPEX-1403 Raman spectrometer with 200-mW Ar^+ laser excitation at 514.5 nm. The X-ray masks were fabricated with the prepared diamond films as substrates. The corrosion resistance tests of the films were also conducted in 30% KOH solution under 80 °C temperature.

Pinhole defect is one of the characteristic defects of the CVD diamond films formed on the deposition process in regular or irregular shapes. Under high resolution optical microscopy, some uniformly distributed pinhole defects were found in the films we prepared. It could be seen that the dimensions of the pinholes were about micron scale. Figure 1 shows the image of a pinhole in the diamond film we prepared. We could see clearly that most areas of the film were perfect except a pinhole defect was observed in oval shapes. The sidewall of the pinhole was not steep but sloping, and the diameter was increasing from bottom to top. So we can deduce that the defects of the substrate could be associated with the formation of the pinhole defects. Though the defect density was low, the pinholes in diamond films limited the application of the films seriously. Figure 2 shows the SEM image of the deposited diamond films. The crystal grains of the diamond had cubic structure. The dimension of the grains was different. The arrows pointed sites were small cavities in the film, which may form pinhole defects as the diamond films grow.

Figure 3 shows the part of the X-ray mask fabricated with the diamond film we deposited. The pattern of the mask was a grating made up with gold absorbers. And the line width was about 0.5 μm. From the image we could also see a pinhole defect on the diamond film, and the gold grating was destroyed because of the pinhole. So the pinhole is the catastrophic defect in fabricating

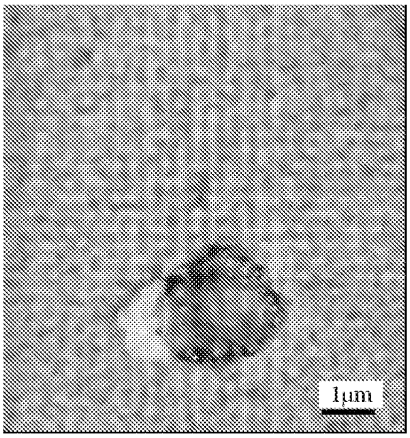

Fig. 1. Micrograph of the pinhole defect in diamond film.

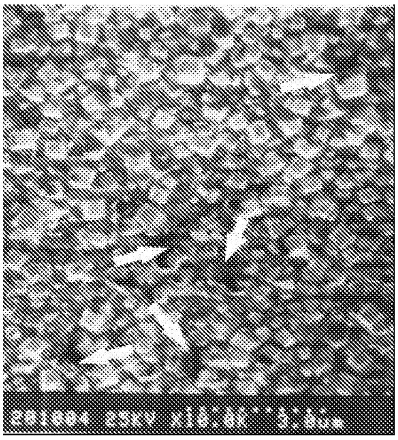

Fig. 2. SEM image of the diamond film.

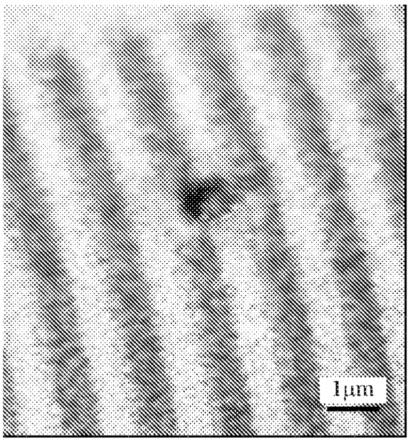

Fig. 3. Micrograph of the X-ray mask destroyed by the pinhole defect.

the ULSI devices in microelectronic technology.

The corrosion resistance tests of the diamond films were conducted in 30% KOH solution under 80°C temperature. In etching process, we found the film cracked and gas bubbles rose from the film's surface for a short while. Then the film delaminated here and there from the substrate. The gas was identified to be H_2, which generated because of the reaction between the KOH solution and silicon substrate. This process was expressed as the following equation[2]

$$2\mathrm{OH}^- + 2\mathrm{H_2O} + \mathrm{Si} \rightarrow \mathrm{SiO_2(OH)_2^{-2}} + 2\mathrm{H_2} \uparrow . \qquad (1)$$

Figure 4 shows the image of the film after etching, and the SEM image of the etched site is shown in Fig. 5. All the cracking sites were round in shape. The white sites in the photograph were the cracking film fragments but still on the substrate, and the black ones were the sites where the cracking films fragments had fallen off. And there are some small concavities in the cracking sites on the silicon substrate, while other areas were smooth. Generally speaking, diamond has good corrosion resistance for alkali or acid. So the cracking reason of the film in our study must be associated with the pinhole defects in the films. When the solution penetrated the thin film through pinholes and reacted with the silicon substrate, the generated H_2 gas broke down the films.

The origins about the pinhole defects in diamond thin films are not very clear. From the image of the pinholes mentioned above we can deduce that the defects on the substrate such as the screw dislocation, edge dislocation and the contamination all could be the origins of the pinhole defects, and some reports had identified these in other films[3]. Because silicon and diamond had the same lattice structure, when diamond film deposited on the silicon substrate, these defects possibly continued in the film and the pinhole defect formed. Lattice mismatch dislocation may also be a factor that affects the formation of the pinhole. The lattice constants in diamond and silicon are 0.3567 and 0.5430 nm, respectively[4]. When diamond film is deposited on the silicon substrate, it is thought that the lattice constant expands in diamond layers and contracts in silicon layers because of the lattice mismatch. Then the lattice aberrance leads to the pinhole defect.

On the other hand, we suppose the formation of the pinholes could be associated with competitive growth among the multi-phase in diamond films. Because the MPCVD diamond's growth is in the sub-stability zone of diamond phase, the carbon atoms and clusters with sp^2 type bond are easy to nucleate than those with sp^3 type bond of diamond. So in MPCVD diamond films, both diamond and non-diamond component exist all together. Diamond belongs to the crystal system of tetrahedral

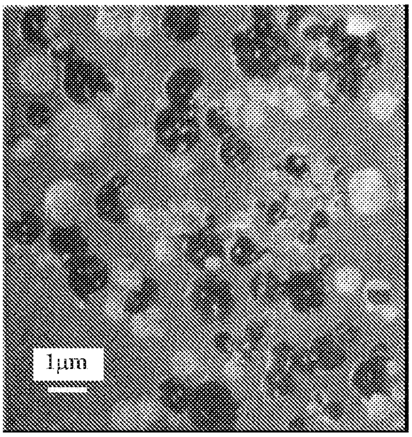

Fig. 4. Cracking image of the diamond film.

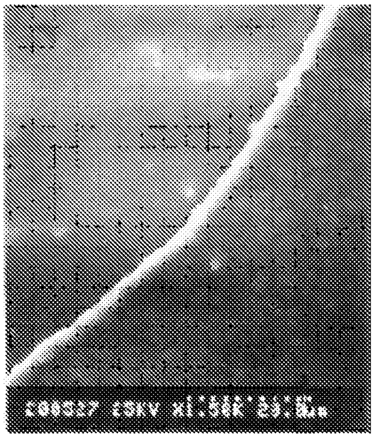

Fig. 5. SEM image of the cracking site on the film.

structure with sp^3 type C-C bond, while graphite belongs to the crystal system of plane and layer structure with sp^2 type C-C bond. The structural differences between the diamond and non-diamond carbon lead to the difference of their Raman scattering spectra. Figure 6 is the Raman scattering spectrum of the diamond film. The Raman spectrum consists of three components, which can be identified as broad peak of amorphous diamond-like centered at about 1530 cm^{-1}, a characteristic diamond line peak at about 1332 cm^{-1}, and a detectable background which can be associated with non-diamond carbon, and the disorder peak has been identified by scattering from the edge of the Brillouin zone due to the effect in microcrystalline graphite[5−7]. It has identified that the intensity of the characteristic diamond peak in Raman spectra strongly associated with the purity of the diamond in films, so we can deduce the purity of the diamond from the spectra with[8]

$$P_{\mathrm{D}} = 75I_{\mathrm{D}}/I_{\mathrm{G}}/1 + 75I_{\mathrm{D}}/I_{\mathrm{G}}, \qquad (2)$$

where P_{D} is the purity of the diamond, I_{D} and I_{G} are the intensity of diamond line peak and graphite line peak respectively. For hydrogen atom has stronger etching effect on graphite than that of diamond, H_2 was used to restrain the growth of the graphite in deposition system. In the early stages of diamond formation, there should be many graphite components in diamond grain boundaries, then the graphite could be etched by hydrogen atoms and formed diamond. Because lattice coefficient of the diamond is smaller than that of the graphite, the volume will be changed with the phase changing, and many voids may be formed (Fig. 2). Because of the migrating of the atoms in high temperature, the small voids will gather together, and then the pinhole forms. The studies carried out by Zhou *et al.*[9] have identified the hydrogen relating to the defects in CVD diamond using EPR technique.

Pinhole defect is one of the main factors that influence the application of the diamond films. In this article the pinhole defects in the diamond films were discussed above. We discovered that the diamond films with pinhole defects have lower corrosion resistance. And it may origin from many reasons such as the screw dislocation, edge dislocation or other defects in substrate. And the lattice mismatch between the substrates and films may also be the factor about it. By the investigation and analysis we also supposed the competitive growth among multi-phase in diamond films may be the real reason for the pinholes' formation in film deposition process. So the results were obtained from our study as following:

(1) Diamond films with pinhole defects have lower corrosion-resistance.

(2) The defect-free wafers should be chosen as substrates to the film deposition.

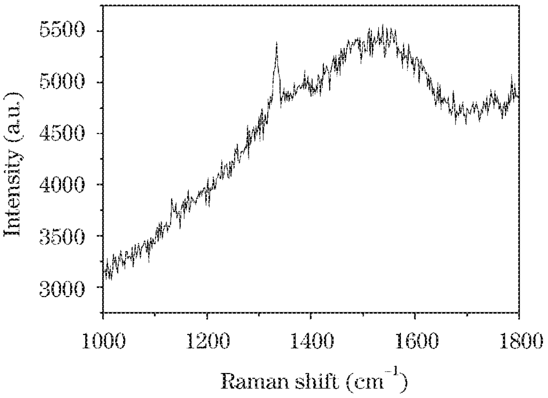

Fig. 6. Raman spectrum of the diamond film.

(3) Proper deposition conditions also should be chosen to prevent the formation of the microcrystalline graphite, which may be associated with the pinhole defects formation.

The real reasons of the pinhole defects formation in MPCVD diamond films are still not very clear at present, and the further study should be made to make clear the factors related to the pinhole formation. The techniques also should be developed to reduce the density of the pinhole defects.

We would like to thank Mr. F. Q. Li and C. Y. Xu who did a lot of work in our SEM and Raman spectra measurements. D. Zhang's e-mail adress is zdp@mail.siom.ac.cn.

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