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Selective growth of diamond by hot filament CVD using patterned carbon film as mask

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Abstract Selected-area deposition (SAD) of diamond films was achieved on silicon substrates with carbon film mask by hot filament chemical vapor deposition. Needle tip scraped lines were used to grow diamond films. Scanning electron microscope (SEM) investigation demonstrates that highly selective and sharp edged diamond films were produced. The results also demonstrate that the proper substrate temperature is very important for diamond selective growth in this deposition process. Since the enhancement of diamond growth was not observed on the needle tip scraped area of Si wafer with diamond powder scratching, the selective growth was considered to be closely correlated to silicon carbide formed during carbon film deposition and the residual carbon in the scraped area.

Key words Diamond film, Selective deposition, Hot filament CVD, Carbon mask

CLC numbers TN304.1^{+}8, TN304.055

1 Introduction

Diamond is a promising material for thermal management and microelectronic devices, due to its favorable properties of large band gap, high mobility of electron–hole pairs, and high thermal conductivity[1,2]. However, it is very difficult to pattern diamond using traditional technologies, such as chemical or physical etching, which can sometimes be done in an extreme environment that few masking materials are suitable to withstand. Area-selected deposition as a bottom-up method can produce diamond patterns with high quality and efficiency[3-5]. And selective growth of diamond film has been used as an alternative to diamond etching to produce the patterns.

Since Hirabarashi *et al*[5] reported the first selective deposition of polycrystalline and single-crystal diamonds using successive roughening and patterned etching of silicon wafer, many methods have been developed to achieve selective diamond growth, such as selective laser annealing of silicon wafer scratched by diamond powder[6], selective growth of diamond film with patterned SiO_2 as a mask[7] and diamond selective growth on insulators by selective seeding with a double-layer mask[3]. Applications of the methods, however, are hindered by their expensive equipment and complex processes.

In this paper, we report a new approach in which a carbon coated silicon substrate is scraped by a needle to create line-shaped pattern for selective growth of diamond. The method's high selectivity and capacity to produce complex diamond pattern was verified, and the diamond nucleation mechanism was discussed.

2 Experimental

The experiment was performed on a hot filament chemical vapor deposition (HFCVD) system built by our group. The filament is a 0.5 mm coiled tungsten wire heated by DC power to about 2000℃. The chamber was evacuated to 1×10^{-2} Pa before gases were

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introduced into it with a total gas flow of 100 sccm using separate mass flow controllers. The filament was heated when vacuum of the chamber decreased to a preset value.

The substrates [*n*-typed Si (100)] were placed 8 mm below the filament on a Mo substrate holder. A thermocouple monitored the substrate temperature. To enhance the diamond nucleation, the substrates were ultrasonically scratched in a suspension of diamond powder of 0.5 μm.

The samples were prepared in three steps. Firstly, a carbon film was grown with HFCVD on the silicon wafer scratched by diamond powder. This process lasted 30 min at 400 Pa and 600℃ of the substrate temperature, with the ratio of methane to hydrogen being 3%. Secondly，the carbon film was scraped by a sharp needle tip, and the ultimate diamond pattern was decided by the process. Thirdly, the silicon wafers with carbon film patterns were deposited with diamond film in the chamber in 120 min at 400 Pa and 650℃ of the substrate temperature, with the ratio of methane to hydrogen being 2%.

Morphology of the diamond films was observed by scanning electron microcopy (SEM LEO, 1530VP), and the film quality and phase purity were determined by micro-Raman spectroscopy (Dilor LabRam-1B). The Raman spectra were obtained using an Ar^+ laser of 632.8 nm in wavelength and approximately 1 μm in spot size.

3 Results and discussion

SEM image (Fig.1a) of the patterned diamond film deposited at 650℃ shows a line-shaped diamond pattern of about 30 μm in width. The diamond film grew in just the area of the silicon substrate where the carbon film had been broken by the needle tip in the second step, while almost no diamond grew on the carbon film. This means that highly selective deposition of diamond was achieved. An SEM image of high magnification (Fig.1b) for boundary area of the diamond film confirms that the diamond was just grown on the naked area, with very sharp boundary. The clear diamond facets in the SEM image indicate the high quality of the diamond.

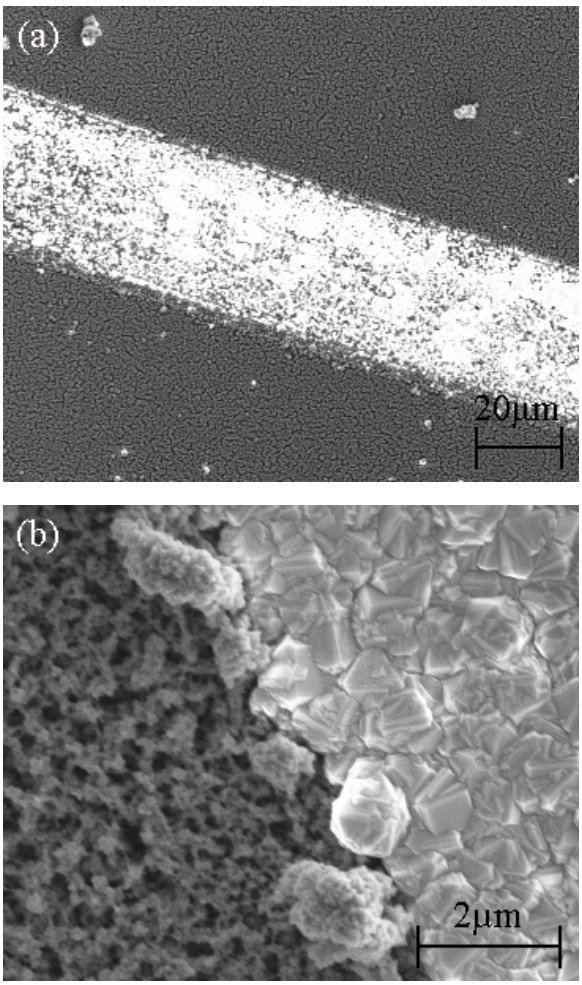

Fig.1 SEM image of diamond film with a line-shaped pattern in width of about 30 μm (a) and high magnification SEM image of the boundary area of the pattern (b).

Patterns of the diamond films are defined in the second step. In order to verify that complex patterned diamond films can be produced with this method, cross-shaped and narrow line-shaped diamond growth area were defined in the second step followed by HFCVD growth. The cross-shaped diamond film in Fig.2a is sharp in edge and good in selective growth, indicating that developing diamond films of complex patterns are feasible with even sharper scraping tools. In Fig.2b, one finds a narrow line-shaped diamond line of only about 2 μm in width, which is very close to the size of diamond grains. The line width of the as-produced diamond line is comparable to that of diamond patterns produced in other bottom-up methods[3,5,6], indicating this method is effective in diamond patterning.

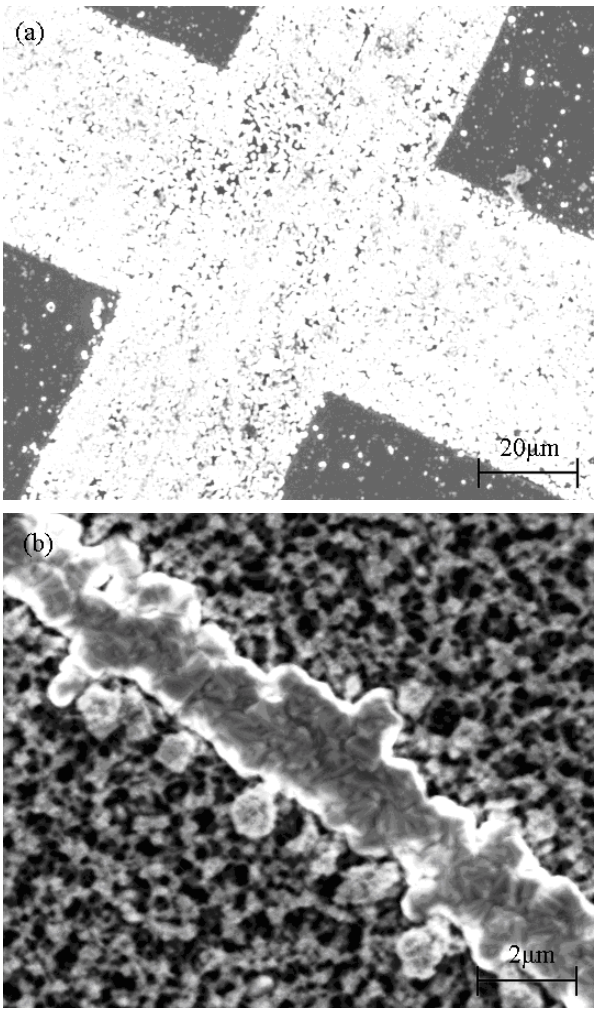

Fig.2 Diamond films with cross-shaped (a) and narrow line-shaped (b) pattern in width of about 2 μm.

Fig.3 shows SEM images of three different samples: Sample A (Fig.3a), diamond film deposited on silicon wafer scratched by diamond powder; Sample B (Fig.3b), the deposited diamond film on diamond powder scratched silicon wafer with needle-scraped pattern; and Sample C (Fig.3c), carbon film scraped by the needle. The diamond film of Sample A is not so continuous after two hours of HFCVD, but the nucleation density is much higher than that on the carbon film, whereas nucleation density in the needle-scraped area in Fig.3b was apparently low. These indicate that the needle scraping on silicon wafer scratched by diamond power would prohibit the diamond nucleation, rather than enhance it. Fig.3c also shows that most of carbon film was removed while a small fraction of carbon remained in the needle- scraped area.

The selective diamond growth may well be affected by the substrate temperature. This can be seen with a sample prepared in the same condition as above but at 750℃ of the substrate temperature for HFCVD growth. As shown in Fig.4, the film growth is not good, with diamond crystals on the mask, though the nucleation density is much higher in the needle-scraped area.

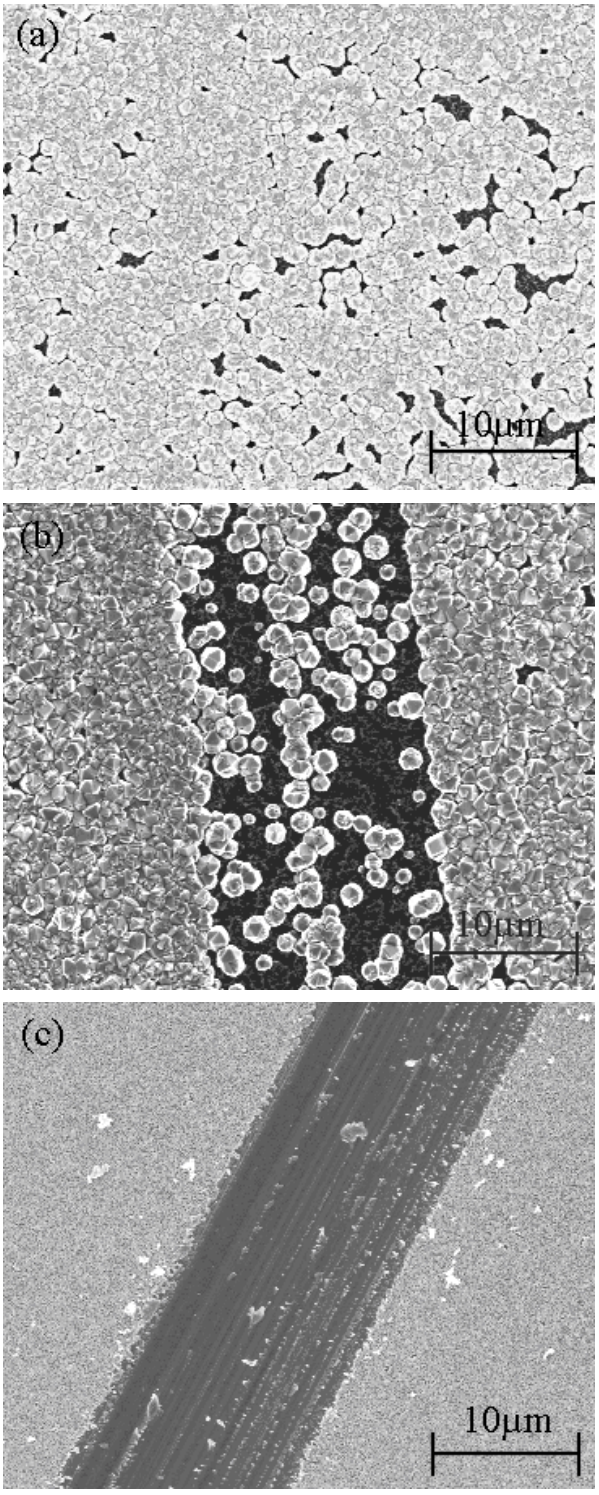

Fig.3 SEM images of diamond films deposited on silicon wafer scratched by diamond powder (a), the deposited diamond films with needle–scraped pattern on silicon wafer scratched by diamond powder (b) and carbon film scraped by the needle (c).

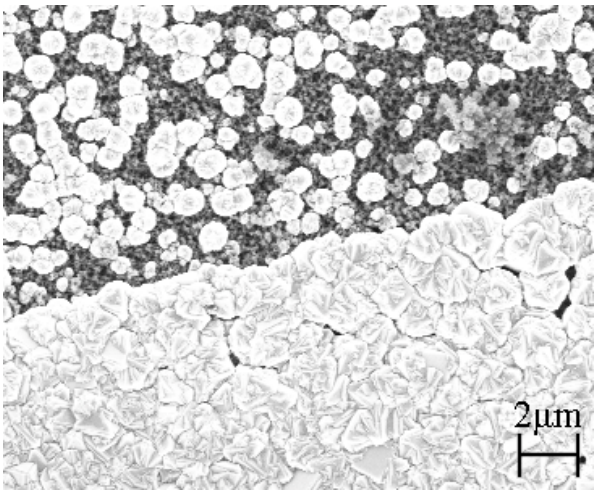

Fig.4 SEM image of diamond film deposited on substrate at 750℃.

Fig.5 shows the Raman spectra of the patterned diamond film (A) and the carbon mask of the sample (B) in Fig.1. The peak at 1333.4 cm^{-1} attributes to diamond[8]. The peaks at 1511.0 cm^{-1} and 1605.0 cm^{-1} could be G bands of mixture of various disordered carbon particle embedded in the diamond film[9]. As visible Raman spectroscopy of the sp^2 sites is 50~230 times more sensitive than the sp^3 sites the content of disordered carbon is very low in the diamond film. The peaks at 1329.8 cm^{-1} and 1595.5 cm^{-1} are typical peaks of D and G band of carbon film, indicating that the mask layer is disordered carbon[9].

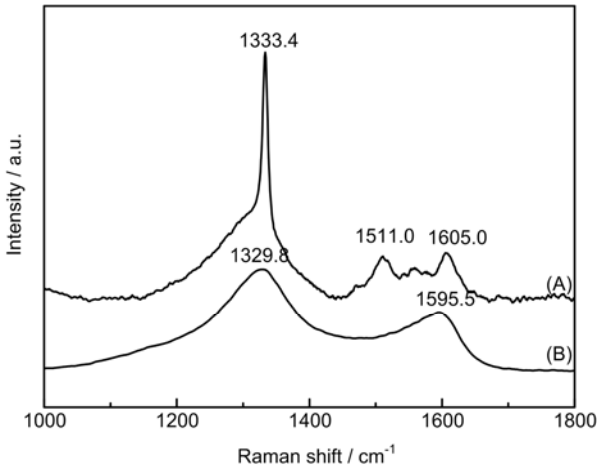

Fig.5 Raman spectrum of selectively deposited diamond film (A) and Raman spectrum of carbon mask (B).

In general, the nucleation density contrast between scratched silicon wafer and carbon film revealed that as-prepared carbon mask is good for selective diamond growth. Although many researchers found that intermediate layer could enhance diamond nucleation on silicon wafer[10-12], the intermediate layers reported are no more than 20 nm[13], which is much thinner than the carbon layer in this work. Feng *et al*[14] studied diamond nucleation densities on carbon films of various thicknesses and observed the nucleation density of about 10^6 cm^{-2} on carbon films of thinner than 1 μm and very low nucleation densities on carbon films thicker than 1 μm. The effect of the carbon film thickness on diamond nucleation can be explained by etching rate of carbon films exposed to hydrogen plasma. At high temperature, the etching rate is much higher than that at lower temperature. Some area of the as-deposited film could be etched by the hydrogen plasma at 750℃. The thick carbon film acted as a mask covering the diamond nucleation sites which produced in the scratching process[15,16] and prohibited the diamond nucleation on unwanted area.

In contrast, the nucleation in the area scraped by the needle tip in Step 2 is quite high. Scrape as a method of producing defect to enhance nucleation of diamond on silicon wafer has been reported by many teams. However, scraping on silicon wafer ultrasonic scratched by diamond powder, has a negative effect (Fig.3b). That is because that the scraping removed the diamond seeds remained on the silicon wafer by scratching process and changed the defects types as well. Nevertheless, by scraping carbon film covering the silicon wafer, the nucleation density on the scraped area would be as high as on silicon wafer scratched by diamond powder. We believe that this is because in the scraping process many carbon residuals and silicon carbide formed during carbon film deposition remained on the scraped area. The graphite edges were believed to be a very important kind of diamond nucleation site[17,18] and silicon carbide can enhance the diamond nucleation[19-21].

4 Conclusions

A new method has been developed for selective diamond growth. High selectivity and sharp edged line and cross patterns of diamond films were obtained. It was proved that the substrate temperature is important for selective diamond growth in the deposition process. The nucleation enhancement on the scraped area of carbon film covered the silicon wafer and the decreased nucleation on scraped area of silicon wafer

scratched with diamond powder were observed. The graphite edges existed in carbon residuals after the scraping and the silicon carbide formed during carbon film deposition were believed to be responsible for the diamond nucleation enhancement in the scraped area.

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