SELECTIVE DEPOSITION OF DIAMOND CRYSTALS BY HOT-FILAMENT METHOD

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Spatially selective deposition of polycrystalline and single-crystal diamonds has been achieved on a silicon wafer by chemical vapor deposition from CH₄ and H₂ gases using a hot-filament method. Before deposition, nucleation sites are formed by roughening the substrate surface by fine diamond particles, followed by drawing a resist pattern on the substrate and successively etching the surface by an Ar⁺ ion beam. The nucleation of diamonds occurs selectively on the roughened area.

1. Introduction

Recently, the chemical vapor deposition of diamond has been studied by many researchers, as reviewed in Ref. 1). However, these products are polycrystalline films or particles with crystal habits grown randomly on a substrate. If one could spatially control the deposition of diamond crystals and their size, the number of practical applications for diamond would increase tremendously. In this paper, we report the selective deposition of polycrystalline and single-crystal diamonds.

For spatially selective deposition, two surface areas are required on which the nucleation density of a deposited material differs by several orders. Previously, silicon³, titanium disilicide³, tungsten⁴, etc. were deposited selectively by fabricating two materials on a substrate on which the nucleation density of the deposited material differs greatly. Furthermore, single-crystal silicon has been grown selectively on amorphous Si₃N₄ in the presence of SiO₂⁵. There has also been a report of aluminum grown selectively using a photo-chemical reaction which occurs only in the limited area radiated by a laser beam⁶.

For the selective deposition of diamond, we have used two conditions of the substrate surface. We have used the well-known high nucleation density of a Si substrate roughened by fine particles, such as diamond or silicon carbide, an increase by several orders of magnitude compared with an untreated and smooth substrate⁷. This method uses two different surface states for the selective deposition and is completely different from those mentioned above. Since it is impossible to control the shape and size of the area to be roughened on a micron scale, we have first drawn resist patterns on a roughened substrate and successively etched the substrate using an Ar⁺ ion beam to decrease the nucleation density of the area surrounding the resist patterns. The resist is removed before the deposition of diamond and diamond crystals grow selectively on the area that was covered.

2. Experimental procedures

Nucleation sites were fabricated on a silicon wafer with (100) orientation as follows. First, the silicon wafer was roughened in ethyl alcohol containing 15–30 μm fine particles of diamond using an ultrasonic cleaner for one hour. After cleaning the silicon wafer in ethyl alcohol and acetone solution resist patterns (OEBR-1000 and OEBR-100, Tokyo Ohka Kogyo Co. Ltd.) were drawn on the roughened substrate by photo-lithography and electron-beam lithography. The substrate was then etched by an Ar⁺ ion beam at room temperature and a pressure of 2.7×10⁻² Pa, using an accelerating voltage of 0.5 kV and a current density of 0.45 mA/cm². After removing the resist with acetone, the substrate was cleaned in a mixture of H₂SO₄ and H₂O₂, followed by an immersion in HF solution. Diamond was deposited on the wafer by

3. Results

The dependence of the nucleation density on the etching depth by the Ar⁺ ion beam is shown in Fig. 1. The definition of nucleation density is very difficult, since the observation of the initial nucleation events is undetectable within the resolution limit of available electron microscopes. We define the nucleation density of diamond as the number of crystals displaying clear (100) and (111) facets per unit area of the film surface. As can be seen in Fig. 1, the nucleation density of the roughened surface using the above definition is 1–2×10⁶/mm², which decreases monotonically with the etching depth and becomes about 10⁴/mm² at a 200 nm etching depth. For comparison, the nucleation density on an untreated silicon wafer is less than 10⁴/mm². To induce the selective deposition, the large difference in the nucleation density dependent on the etching depth was used as follows.

An example of a resist pattern drawn by photolithography after roughening a silicon substrate is shown in Fig. 2a. The lines are 1.5 µm in width and 37.5 µm in length. The etching depth on the area surrounding the resist pattern was 100 nm, which gave a nucleation density 10⁶ smaller than that on the silicon roughened by fine diamonds for an hour. The line edges are neither straight nor sharp, but that is not crucial for our purpose.

A photograph of the polycrystalline diamonds deposited on the substrate in Fig. 2a is shown in Fig. 2b using a scanning electron microscope, equipped with a field-emission gun (FE-SEM). The selectivity is fairly good. Only one failure in selectively is observed between the first and second lines from the right. The line width is rather wider in Fig. 2a, reflecting the lateral growth of diamond crystals from nucleation sites.

The next step in the selective deposition is to produce single-crystal diamonds by adjusting the size and spatial period of the nucleation sites. From the nucleation density of 1–2×10⁶/mm² on the roughened silicon surface under our experimental conditions, we estimated the optimum pattern size of 0.8–1 µm diameter for a single-crystal nucleation. Experimentally, the resist pattern of 1 µm diameter and 10 µm spatial period was formed on a roughened silicon substrate by electron beam lithography. The result is shown in Fig. 3. The nucleation sites are completely occupied by diamond particles. However, the proportion of diamond particles grown at positions outside nucleation sites (random diamonds) to those grown at nucleation sites (selected diamonds) is 0.05. The size of the random diamonds is rather smaller than that of the selected diamonds, which are 4–6 µm in diameter. An enlarged FE-SEM photograph of Fig. 3 is shown in Fig. 4 to show the characteristics of each crystal. As can be seen, cubo-octahedral crystals and multiply twinned crystals are the main products. Some polycrystalline particles which seemed to originate in the initial stage of the nucleation are also observed. Furthermore, many secondary nuclei grow on facets of the deposited
Fig. 2.  a: An FE-SEM photograph of a resist pattern drawn by standard photo-lithography after roughening a silicon substrate. b: An FE-SEM photograph of polycrystalline diamonds deposited selectively on the pattern in Fig. 2(a) after removal of the resist.

Fig. 3.  Single-crystal diamonds deposited on nucleation sites.

Fig. 4.  An enlarged FE-SEM photograph of Fig. 3.
crystals and become one of the causes for the deterioration of the quality of single crystals.

Raman spectra and electron diffraction were measured to identify deposited products and their quality. The electron diffraction pattern of the selectively deposited polycrystalline product corresponds to that of diamond. Micro Raman spectra of a polycrystalline film and an isolated single crystal are shown in Figs. 5a and 5b. The lines at 1333 cm\(^{-1}\) and 1560 cm\(^{-1}\) correspond to the vibrations of diamond and graphite, respectively. The strong-intensity background is attributed to the fluorescence, which probably originates in crystal boundaries, since about 15 crystal habits are observed in the laser beam diameter of 4 \(\mu\)m. On the other hand, the Raman spectrum of an isolated single-crystal displays only one sharp line at 1333 cm\(^{-1}\) of the diamond first-order phonon as shown in Fig. 5b. Since the size of the laser beam and the single crystal are almost the same, the Raman spectrum of Fig. 5b is that of a single-crystal diamond.

4. Discussion

The selective deposition of diamond has been achieved by using the difference in the nucleation density of two surface states. The selectivity of polycrystalline diamond is good, but that of single-crystal diamond is incomplete due to the lack of single-crystallinity and the failure in growth position selection. These problems could be resolved by adjusting the nucleation density, the pattern size and conditions of diamond deposition.

Generally, crystals grow through the processes of nucleation, coalescence and successive growth. The mechanism of nucleation is a very interesting problem. However, it is not presently clear why the nucleation density on the roughened surface is higher than that on the untreated one. The roughened surface is composed of small pits, sharp edges, strains, mosaic structures and so on. These structures may contribute to the nucleation process in a complicated way. Observations of lattice images of a cross-sectional view of the etched surface of silicon using an electron microscope\(^9\), show that the role of Ar\(^+\) ion beam etching seems to remove the mosaic layer for the formation of nuclei, and to round off the sharp edges of the scratches. By Ar\(^+\) ion beam etching, the mosaic layer is easily removed, whereas strains still remain. It is not obvious whether strains exist before the preparation of a thin sample for a cross-sectional observation.

While clear crystal habits are observed on the outside of these crystals, stacking faults along the (111) direction are also frequently observed. Comparison of the two Raman spectra in Fig. 5 indicates that crystal boundaries are the origin of the fluorescence. It is possible that the 488 nm wavelength of the Ar\(^+\) ion laser excites electronic fluorescence of double bonds, triple bonds, radicals or defects which may exist in these boundaries. To make high quality diamonds, these boundary problems need to be solved. Further, detailed observations of the boundaries between the substrate and a grown crystal, and between crystals or unstable nuclei at the early stages of nucleation should be helpful in understanding the nucleation mechanisms.

In conclusion, polycrystalline and single-crystal diamonds have been selectively deposited on a silicon wafer by the combination of roughening the substrate surface and etching the surface by an Ar\(^+\) ion beam. The selectivity of polycrystalline
diamonds is fairly good. However, a failure in the growth position selection is observed for the selective deposition of single-crystal diamonds. Further work on the improvement of single-crystal deposition is in progress.

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