Deposition of diamond films on sapphire: studies of interfacial properties and patterning techniques

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Abstract

Polycrystalline diamond films were grown on single crystal sapphire substrates using hot filament chemical vapour deposition (CVD). Problems with poor adhesion, stress and film cracking became severe for deposited areas greater than about $(100 \, \mu m)^2$. Scanning electron microscopy analysis showed the films to be failing both at the interface and in the diamond layer itself. Transmission electron microscopy cross-sections of the interface showed that the interface was clean and free from non-diamond carbon impurities. Spallation problems in the diamond film could be reduced by introducing a barrier layer of epitaxial silicon grown on the sapphire prior to the diamond CVD step. Patterned silicon-on-sapphire wafers were then used as substrates for CVD of diamond in order to define features of linewidth more than 10 μm in the diamond films. Two methods were used: selective nucleation and lift off.

1. Introduction

Growth of diamond thin films by chemical vapour deposition (CVD) is now a very active area of worldwide research [1,2]. One potential application of diamond films is in the field of electronic devices [3,4], since doped diamond shows useful semiconducting properties. Proposed heteroepitaxial devices, to date, utilise silicon as the bulk substrate material onto which doped diamond is deposited. Other possible substrates, such as single-crystal sapphire, have received much less attention. Sapphire has been used previously in the semiconductor industry to produce silicon-on-sapphire (SOS) devices [5, 6]; these have many advantages over bulk Si devices, including that of being radiation hard. Diamond-on-sapphire (DOS) devices may be even more resistant to radiation damage than SOS devices. Thus an investigation of potential problems, especially of the interface between CVD-grown diamond and sapphire, is urgently required. Furthermore, methods need to be devised to pattern DOS films into the required device structures with resolutions comparable to those used in modern Si technology, typically linewidths of a micrometre or less. Patterning of diamond films grown on Si has been attempted by a number of workers [7–11] with varying degrees of success, but patterning of DOS has yet to be successfully demonstrated.

Unfortunately, all attempts of diamond CVD on sapphire reported to date have met with, at best, limited success [9, 11]. Thermodynamically, sapphire is a very stable structure; its conversion from Al_2O_3 to an intermediate carbide layer is particularly unfavourable. The lack of any carbide "glue" layer at the diamond–sapphire interface makes for poor adherence of diamond films. What adherence there is can also cause problems, since sapphire has a much higher coefficient of thermal expansion than diamond, which can cause stresses to develop in the diamond layer on cooling. We investigate these points in more detail in the present paper.

2. Experimental details

Diamond was deposited using a standard hot filament CVD apparatus, with a 1 vol.% methane in hydrogen gas mixture. The process pressure was maintained at 30 Torr, with the total gas flow rate being 200 sccm. The Ta filament was maintained at a temperature of about 2000 °C and positioned about 5 mm above the substrate. This heated the substrate to a local surface temperature of about 900 °C. This system has previously been used to grow good quality polycrystalline diamond films on Si substrates with a growth rate of about 0.5 $\mu m \, h^{-1}$ [12].

The single crystal sapphire (01$\bar{1}$2) substrates were manually abraded with 1–3 μm diamond powder prior to deposition in order to promote nucleation sites. Without this abrasion initial diamond growth rates were negligibly small.

For the patterning experiments, commercially available SOS wafers were used. These consisted of a 0.4 μm layer of epitaxially grown Si on sapphire substrates. Patterning was attempted using two separate techniques (Figs. 1 and 2). In selective nucleation (Fig. 1), the Si layer is first etched using standard photolithographic and reactive ion etching methods to expose regions of sapphire. The patterned SOS sample is then gently abraded using an ultrasonic bath of aqueous diamond slurry. This produces ample nucleation sites on the softer Si areas, but the harder exposed sapphire areas remain relatively undamaged. Subsequent diamond growth then occurs preferentially on the Si areas.

Conversely, in the lift off technique (Fig. 2), the patterned SOS samples are abraded thoroughly to produce nucleation sites equally on the Si and sapphire areas. CVD now results in a uniform coverage of diamond over the entire sample. Subsequent use of a chemical etching agent to remove the Si areas removes the overlaying diamond in a lift off process, leaving only areas of diamond on sapphire.
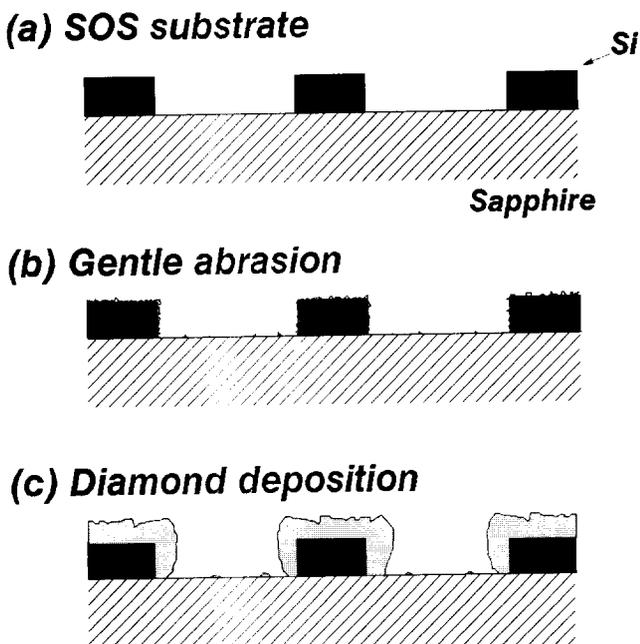
(a) SOS substrate

Fig. 1. Patterning DOSOS films by selective nucleation. (a) The SOS substrate is patterned by dry etching the Si layer. (b) Gentle ultrasonic abrasion using an aqueous diamond grit slurry produces nucleation sites preferentially on the soft Si areas and not on the harder sapphire regions. (c) Diamond deposition causes continuous films to form preferentially on the Si regions, producing patterned DOSOS tracks.

(a) SOS substrate

(b) Thorough abrasion

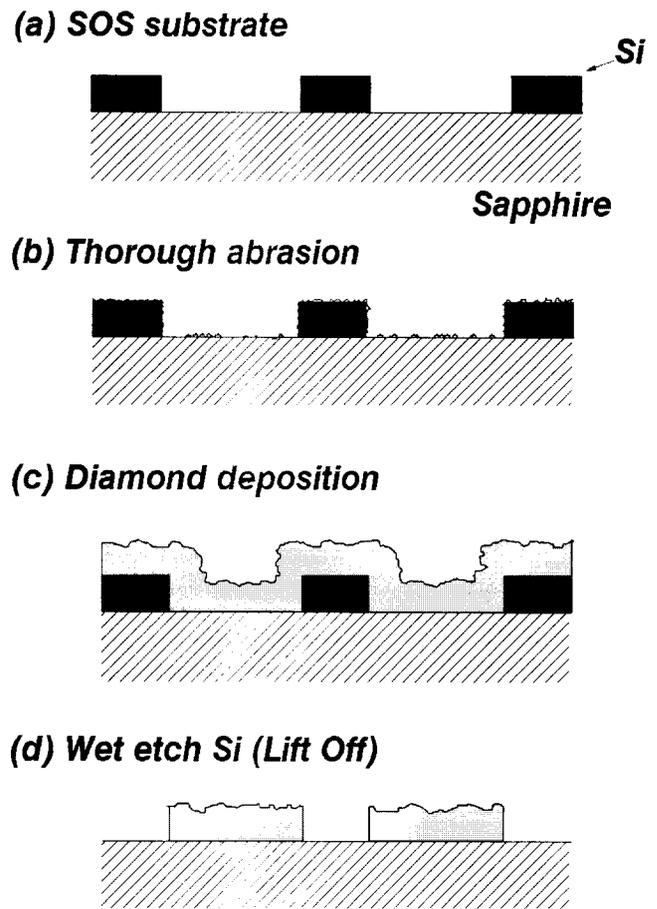## (c) Diamond deposition

(d) Wet etch Si (Lift Off)

Fig. 2. Schematic diagram of the lift off method to produce patterned DOS. (a) The SOS is patterned using dry etching techniques. (b) Thorough abrasion promotes nucleation sites on Si and sapphire areas equally. (c) CVD produces a continuous diamond film over all areas. (d) Wet etching removes the underlying Si, leaving patterned DOS.

3. Results

3.1. Growth of diamond on sapphire

Diamond was found to grow on sapphire in our CVD reactor at a rate comparable to that on Si, *i.e.* about 0.5 μm h^{-1}. Diamond was confirmed as the dominant carbon phase using laser Raman spectroscopy, although the 1332 cm^{-1} peak was observed to be shifted to 1338 cm^{-1}, presumably as a result of thermally induced stresses between the diamond and sapphire [13]. The effect of these stresses was found to be dependent upon the area of continuous diamond film: films greater in area than about (100 μm)^2 often cracked and crazed into plates, with both trans- and intergranular cracks visible (Fig. 3). Moreover, poor adhesion of the film in these areas often caused the diamond to delaminate as free-standing flakes. Areas of continuous film smaller than about (100 μm)^2, however, remained bonded to the sapphire surface, without cracking.

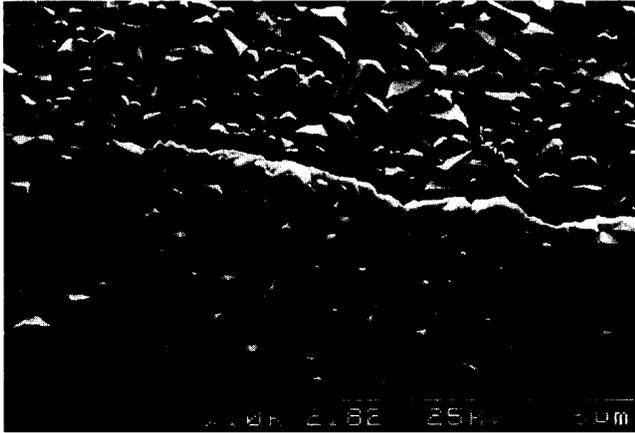This remaining material was examined in cross-section

Fig. 3. Electron micrograph of a polycrystalline diamond film grown on single crystal sapphire. Compressive stresses due to thermal expansion mismatch between diamond and sapphire have caused the film to crack, with the cracks running along the edge of grain boundaries as well as through the grains.

by transmission electron microscopy (TEM), but the sectioning and preparation procedure often caused the diamond film to crack off. Failure was observed to occur both at the interface and in the diamond itself, often leaving behind isolated islands of diamond. Figure 4 shows TEM diffraction contrasts in such an island, highlighting the stresses within the crystal. The interface between the sapphire and the diamond was clean (Fig. 5), with the diamond lattice and sapphire lattice in intimate contact and no evidence for the presence of a carbide or amorphous carbon interlayer. We believe that it is the lack of any suitable "glue" layer, coupled with the high stresses, that weakens the diamond/sapphire interface. Our observations are consistent with the idea that the entire diamond film is attached to the sapphire in a few isolated regions only. These regions are possibly where diamond nucleates inside a crevice on the sapphire surface and then grows outward, wedging the diamond crystal firmly into place; or where residual diamond crystals from the abrasion step remain embedded. Subsequent rapid lateral growth (see below) covers the sapphire surface with diamond, without any chemical bonding between the diamond and sapphire occurring. Delamination of the diamond film is therefore facile, with the whole film flaking off essentially intact, except at the attachment points where the diamond crystals are embedded in the sapphire fracture.

3.2. Growth of diamond on SOS

Diamond grows well on SOS, with the Si acting as a partial stress-relieving layer, although areas of continuous film greater than about $(200 \ \mu m)^2$ still delaminate. This time, however, the weak interface is at the Si/sapphire rather than at the diamond/Si boundary. This problem puts an upper limit on the size of features
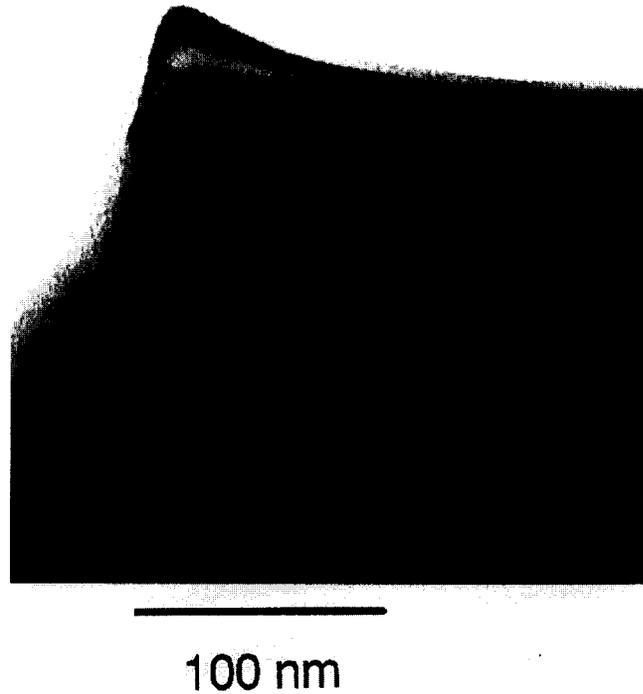

100 nm

Fig. 4. TEM of a cross-section through the diamond/sapphire interface. Two separate grains within the diamond can be seen, with the degree of stress being indicated by diffraction contrast patterns caused by distortions in the diamond lattice.

that could be fabricated using diamond-on-silicon-on-sapphire (DOSOS) technology, although this limit would probably depend upon the thickness of the Si barrier layer.

3.3. Selective nucleation of diamond on SOS

Figure 6 shows that preferential deposition of diamond has occurred on the abraded Si areas, with nucleation on the exposed sapphire regions being considerably reduced. The Si areas are covered in a continuous diamond film, whereas the sapphire areas only show isolated crystal growth. An interesting feature of this micrograph is that it shows that sapphire areas near the Si sidewalls exhibit a much higher growth rate than areas further away. The presence of the vertical wall seems to act as a focus, increasing nucleation in its vicinity. There are a number of possible reasons for this. Electrostatic charging of the sidewall may cause a local increase in the concentration of reactive species. Alternatively, it could be the roughened microstructure of the surface of the sidewall, produced during the dry etching step, that provides suitable sites for diamond nucleation. Whatever the mechanism, this "sidewall

Fig. 5. High resolution TEM cross-section through the diamond/sapphire interface showing the intimate contact between the two crystal lattices without any obvious amorphous interlayer.
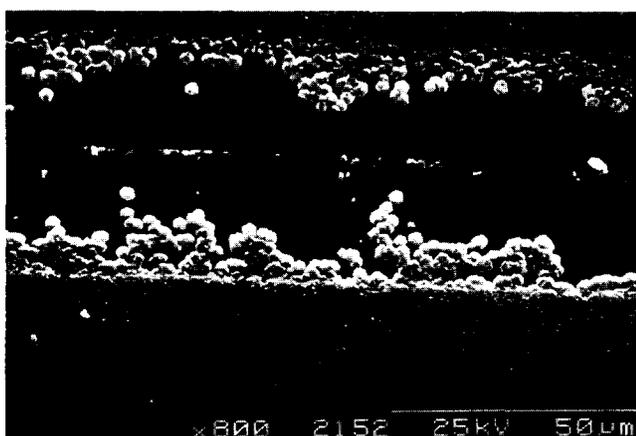

Fig. 6. Electron micrograph of diamond grown on patterned SOS. The stripe is a 50 μm track etched in the Si exposing the sapphire substrate. The diamond nucleation density on the Si areas is much greater than on the sapphire areas, leading to smaller crystals and a continuous film. The sapphire areas show isolated large crystals, with an enhanced nucleation density in the vicinity of the sidewall. This leads to rapid lateral growth, and gradual loss of definition of the pattern.

Fig. 7. Electron micrograph of a (150 μm)^2 square contact pad etched into the SOS, after subsequent diamond CVD. Enhanced lateral growth rates are particularly noticeable at the corners of the feature and in the narrow trench at the centre left of the image.

effect" results in the lateral growth rate being almost an order of magnitude faster than the vertical rate. This is even more apparent in Fig. 7, where the presence of two sidewalls in close proximity at the corner of a feature leads to very rapid sideways growth. This fast lateral growth limits the resolution of patterned lines, since narrow lines are rapidly filled in (Figs. 7 and 8). Selective nucleation may therefore prove a useful patterning method for larger geometry devices, such as sensors, but may be inappropriate for VLSI applications.
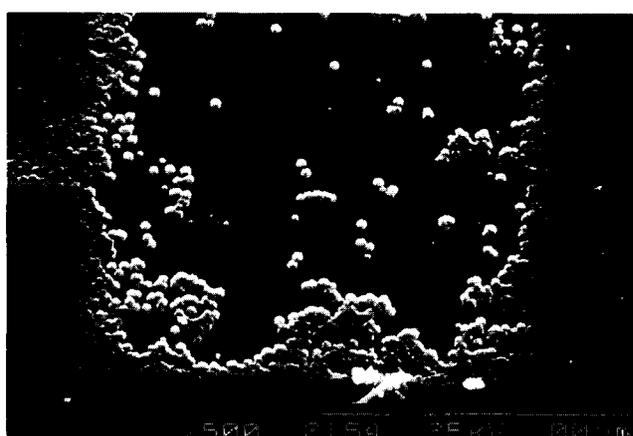
3.4. Lift off

The major problem encountered with this procedure was that the abrasion of the SOS samples did not produce enough nucleation sites on exposed sapphire areas. Of course, it was possible to increase the number of nucleation sites by increasing the abrasion time, but at the expense of severe damage to, and even removal of, the softer protruding Si features.

Small sapphire features could be covered with a continuous diamond film as a result of lateral growth from the sidewalls (Fig. 9), but larger sapphire areas often contained only isolated diamond nuclei. Furthermore, it was found that after removal of the Si by wet etching, the continuous diamond layer covering
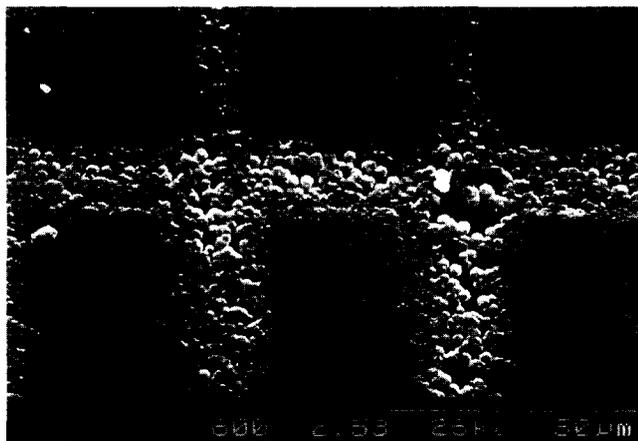
Fig. 8. Electron micrograph of patterned SOS after subsequent diamond CVD. The original linewidths were 10, 15 and 20 μm, showing the complete loss of definition of small features owing to lateral diamond growth.
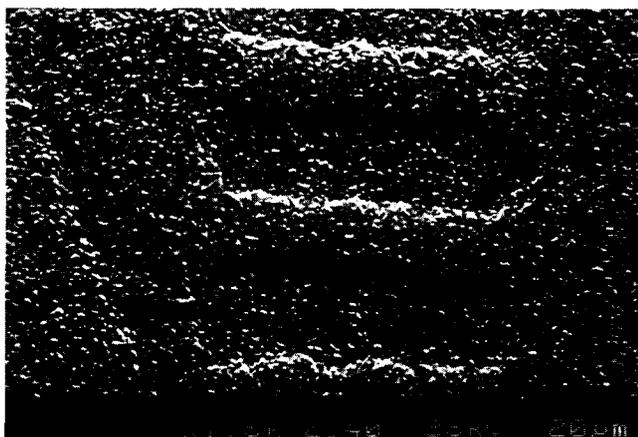

Fig. 9. Electron micrograph showing complete infill of small patterned SOS structures with CVD diamond.

Fig. 10. Electron micrograph of patterned diamond on sapphire, after lift off of the Si layer. The diamond regions are not continuous films; isolated crystals define the pattern. In the upper left corner of the lower feature, the film has become continuous, but as a result the pattern definition has been degraded.

small features often delaminated completely, leaving no pattern. Larger areas, where the diamond had not formed a continuous film, did lift off adequately, and the outline of the mask can be seen in patterns of isolated diamond crystals left behind on the sapphire (Fig. 10). It may subsequently be possible to use these crystals as nucleation points for a pre-patterned DOS film; however this does not look promising as a potential patterning technique owing to its complexity and poor resolution.

4. Conclusions

DOS and DOSOS technology would appear to be challenging, since poor adhesion and stress problems, coupled with the difficulty in patterning, will prove a severe limitation on its use for device applications. One possible solution may be the use of low temperature growth conditions to minimise thermal expansion mismatch during deposition. However, this will only be viable if the deposition rate is not reduced significantly. Another approach may be to utilise barrier layers of, say, Si, of sufficient thickness that stress problems can be alleviated. However, if it transpires that the necessary thickness is of the order of several microns, then any benefits from using DOS may also be cancelled.

Acknowledgments

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