Studies of heteroepitaxial growth of diamond

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Abstract

Large-scale heteroepitaxial growth of diamond depends critically on the development of a suitable lattice-matched substrate system. Oxide substrates, notably MgO and SrTiO\textsubscript{3}, on which thin epitaxial films of iridium serve as a nucleation layer for diamond have already shown considerable promise. We describe here improvements in the growth of single crystal diamond by low-pressure microwave plasma-enhanced CVD. Oxide substrates with flat, low-index surfaces form the initial basis for the process. Iridium was deposited on heated substrates in a UHV electron-beam evaporation system resulting in epitaxial films, typically 150–300 nm thick, with Ir \((100)\) parallel to the surface of all substrates as confirmed by X-ray and electron backscattering diffraction. Following Ir deposition, the samples were transferred to a CVD reactor where a bias-enhanced nucleation step induced a dense condensate that completely covered the Ir surface. Uniform nucleation densities of order \(10^{12}\) cm\(^{-2}\) were observed. Interrupted growth studies, carried out at intervals from seconds to minutes subsequent to terminating the nucleation step, revealed a rapid coalescence of grains. One hour of growth resulted in a smooth, nearly featureless, \((001)\) diamond film. For extended growth runs, slabs of diamond were grown with thickness as great as 38 mm and lateral dimensions near 4 mm. The crystals were transparent in visible light and cleaved on \((111)\) planes along \((1\overline{1}0)\) directions, similar to natural diamond. Of particular significance is the successful use of sapphire as an underlying substrate. Its high crystalline perfection results in epitaxial Ir films with X-ray linewidths comparable to those grown on SrTiO\textsubscript{3}. However, Al\textsubscript{2}O\textsubscript{3} possesses superior interfacial stability at high temperatures in vacuum or in a hydrogen plasma with a better thermal expansivity match to diamond. Since sapphire is available as relatively inexpensive large diameter substrates, these results suggest that wafer-scale growth of heteroepitaxial diamond should be feasible in the near future.

1. Introduction

Heteroepitaxial growth of advanced electronic materials depends on the development of suitable, relatively low-cost, lattice-matched substrate systems. A great deal of progress was made toward heteroepitaxy of diamond with growth of highly-oriented crystallites of diamond on silicon, despite the existence of a large lattice parameter mismatch \([1–3]\). Later, a significant advance was made with the discovery that films of Ir, grown as a buffer layer on MgO, could serve as a substrate for the nucleation and growth of CVD diamond \([4–6]\). With a lattice parameter 7% larger than diamond, Ir appears to have the requisite long-term chemical and physical stability in the high-temperature environment of a hydrogen plasma. More recently, the use of SrTiO\textsubscript{3} as a replacement for MgO has proven useful in decreasing the mosaic spread of the epitaxial Ir and the resultant heteroepitaxial diamond \([7,8]\).

In parallel with heteroepitaxial growth efforts, the conditions for achieving high diamond nucleation densities on various substrates have been extensively examined. The bias-enhanced nucleation process \([9]\), in which a negative voltage applied to the substrate results in its bombardment by relatively low-energy positive ions extracted from the plasma, is a key step for inducing the formation of diamond nuclei. It is important that the nuclei adopt the underlying orientation of the substrate and that their density be maximized, so as to lead to rapid coalescence of crystallites during the early stages of growth. Although the conditions that lead to effective nucleation are well known in principle, there is little

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agreement on the physical mechanisms that underpin the process. The process is also system-specific to some degree, depending on details of reactor geometry and a multitude of processing parameters.

We describe the results of a series of investigations of nucleation and growth of CVD diamond grown on epitaxial Ir. The oxide substrates utilized for Ir growth were predominantly SrTiO$_3$ and Al$_2$O$_3$, although MgO and LaAlO$_3$ were also studied. Care was taken in the preparation and characterization of the low-index substrate surfaces. The nucleation process was optimized to produce high densities, of order $10^{12}$ cm$^{-2}$ across the Ir surface, irrespective of the underlying oxide substrate. The resulting (0 0 1) single crystal diamond films exhibited homogeneity on a scale of millimeters.

2. Experimental methods and results

2.1. Substrates and Ir growth

All experiments were carried out on $5 \times 5 \times 0.5$ mm$^3$ substrates obtained from commercial sources. The (0 0 1) SrTiO$_3$ plates were typically cleaned in buffered HF before insertion into a UHV electron-beam evaporator. After in situ annealing for 20–120 min at 800 °C, Ir was deposited at 2.4 nm min$^{-1}$ to a thickness of 150 or 300 nm. No post-deposition annealing was used as it tended to degrade the (0 0 1) epitaxial Ir. We observed surface reactions of SrTiO$_3$ with stainless steel substrate holders. Reduction of the oxide, as evidenced by its darkening, led to a finite electrical conductance across the substrate. Similar behavior was noted for LaAlO$_3$ but not for MgO.

We also explored Ir growth on polished (1 1 2 0) sapphire, or A-plane $\alpha$-Al$_2$O$_3$ oriented within 0.2 deg of the A-direction. Substrate preparation consisted of annealing in air at 1450 °C for 15 h followed by a light solvent cleaning. The process resulted in atomically flat surfaces, with terraces extending for several micrometers. Ir was deposited at 800 °C under the UHV conditions noted above. The resulting Ir films were epitaxial with orientation Ir(0 0 1)||Al$_2$O$_3$ (1 1 2 0) and Ir[1 1 0]||Al$_2$O$_3$ [1 Î 0 0] [10]. Fig. 1 shows a X-ray diffraction rocking curve for a 300 nm Ir film, confirming the (0 0 1) orientation. We have found that this orientation is stable only if deposited above a threshold substrate temperature near 700 °C. The X-ray line broadening of Ir on A-plane sapphire is comparable to Ir on SrTiO$_3$ [7]. However, the stability of sapphire appears to be higher as no chemical reactions or darkening is observed.

2.2. Nucleation of diamond on Ir(0 0 1)

Following Ir evaporation, the samples were transferred to a CVD chamber with a base pressure of $10^{-7}$ Torr.

The system (2.45 GHz, 6 kW max) contained a quartz dome [11] to confine the plasma to a central region in close proximity to the Mo sample holder. A tungsten bias ring was mounted on posts 32 mm above an electrically isolated sample stage. A typical process was initiated by a pure hydrogen plasma, followed by the addition of CH$_4$ after 5 min, at a 2% methane/hydrogen ratio. System pressure was 18 Torr, with flow rates 6 and 300 sccm for CH$_4$ and H$_2$, respectively, at 700 W microwave power. No nitrogen gas was added intentionally. A bias potential of $-140$ to $-200$ V was applied to the substrate 17 min after starting the process. By interrupting the procedure at times varying from 20 to 180 min we determined that uniform coverage of the substrate with carbon occurred approximately 60 min from the start of biasing. All results described here used a 60 min bias duration. The temperature during bias was approximately 700 °C, as measured by an optical pyrometer focused on the Ir surface. As noted by others, we found the presence of a bright, secondary plasma above the sample to be a necessary condition for achieving efficient nucleation [12–14].

To estimate nucleation density, we interrupted the bias process by terminating the microwave power, leading to rapid quenching of the sample. Examination by SEM revealed regions of high electron emissivity that we interpret to be diamond crystallites at an early growth stage. Fig. 2 shows a result for an Ir/sapphire substrate (in reverse contrast for clarity). We observe a uniform distribution of crystallite sizes with mean linear dimensions 5–10 nm and areal density of at least $5 \times 10^{11}$ cm$^{-2}$. This is a lower bound on nucleation density since some coalescence has already occurred. Furthermore, the distribution, although random, is not far from a
close-packed array. This suggests that the distribution results from "interactions" among nuclei. The liquid-like array leads us to infer that nucleation does not need to occur at special topographic features of the substrate. Careful examination by SEM also reveals that the crystallite shapes, even at this early stage, are faceted with [1 1 0] lateral faces. The uniform distribution of crystallite sizes across the entire surface of the substrate strongly suggests that nucleation begins synchronously with the cessation of bias current.

2.3. Short-time growth and coalescence of diamond on Ir(0 0 1)

At a later stage of growth, the crystallites coalesce to form a continuous thin film. We have carried out studies of coalescence by interrupting growth at intervals from a few seconds to 30 min following cessation of biasing. The CH$_4$/H$_2$ ratio was decreased to 1% following biasing for the following interrupted growth experiments. Fig. 3 shows SEM images of diamond grown on Ir(0 0 1)/SrTiO$_3$ for intervals of 10 and 20 min subsequent to nucleation. They show a surface with a nearly continuous layer of diamond that is penetrated by a network of dark regions composed either of voids or of non-diamond carbon. The dark network is not random but has a structure readily revealed in 2-D Fourier transforms of the images. Since appreciable coalescence has taken place even after 10 min growth, the Fourier transform shows that the network has square anisotropy. Furthermore, the boundaries are predominantly aligned along [1 1 0] directions, as expected for (0 0 1)-oriented cubo-octahedral diamond crystallites. Thus, coalescence must occur by the annihilation of these interfaces, as observed in Fig. 3b. After 20 min, it is clear that the microstructure has coarsened, with appreciably fewer boundaries. This process is reflected by the contraction in reciprocal space of the Fourier transformed image. Square anisotropy is still present but the average grain size, or distance between interfaces, has now increased to ~100 nm.

For a growth time of 60 min, the film is continuous, with thickness 0.15 μm. The surface shows little evidence of the voids or grain boundaries apparent at shorter times. SEM images of the diamond surface are shown in Fig. 4, for a region near the center of the film and for a region at its outermost periphery. The surface is quite smooth with the exception of small features that appear as bright spots. Their average height is a few nanometer as measured by AFM and are most noticeable on fully coalesced surfaces. We suspect that they arise from charging and enhanced emission from slight protrusions on the surface. This is most pronounced when the diamond is highly insulating without low impedance grain boundaries that act as current shunts to the substrate.

Films grown for 60 min have been extensively characterized by X-ray diffraction rocking curves, azimuthal scans, and pole figures. We have also used electron backscattering diffraction to develop pole figures over selected areas ~10 μm$^2$. In all cases, the results are fully consistent with the development of single crystal (0 0 1) diamond, with no evidence for misoriented or twinned regions.

2.4. Long-time growth of diamond on Ir(0 0 1)

To explore the properties of thick diamond films, we have carried out growth for longer periods, from 36 to 48 h. Growth proceeds for 90 min with a CH$_4$/H$_2$ ratio of 1%. Then, the total gas pressure is raised to 28 Torr over a period of 30 min and the CH$_4$/H$_2$ ratio is decreased to 0.75%. We have successfully grown (0 0 1) slabs of diamond with thickness from 25 to 38 μm. The thickest crystals are transparent in visible light and cleave along [1 1 0] directions on (1 1 1) surfaces as observed for natural diamond. Polarized Raman spectroscopy shows that the crystals obey the selection rules expected for light wavevectors parallel to [0 0 1] and [1 1 0] directions in backscattering geometry. Raman linewidths are typically 5–6 cm$^{-1}$, quite good for CVD diamond, but clearly much greater than for natural diamond.

3. Conclusions

We have shown that significant improvements in the heteroepitaxial growth of diamond using a (0 0 1) Ir buffer layer are possible. By optimizing CVD reactor.
Fig. 3. Images of heteroepitaxial diamond growth on Ir(0 0 1)/SrTiO$_3$ for two time intervals after nucleation: (a) 10 min; (b) 20 min. Upper panels: SEM micrographs. Lower panels: 2-D Fourier transforms of the binarized real-space images. The monotonic logarithmic contours are maximum at $k=0$. The Fourier transforms reveal the anisotropic distribution of crystallite interfaces, aligned along Ir[1 1 0] directions. The Ir surface is covered with diamond after 10 min growth (a). Appreciable coalescence occurs by 20 min, as seen by the contraction of the Fourier transform in (b).

geometry and the biasing process, nucleation densities of order $10^{12}$ cm$^{-2}$ have been inferred from quenching experiments. The uniform crystallite sizes provide compelling evidence that nucleation occurs synchronously with the termination of biasing. In the presence of a bias current, the carbon condensate is in a highly excited, nonequilibrium state. Upon removal of the bias, the condensate cools rapidly, initiating nucleation. The liquid-like distribution of crystallites shown in Fig. 2 implies that correlations are induced among crystallites at a very early stage of growth. The most likely scenario is one in which early growth is controlled by depletion of the carbon condensate deposited on the Ir surface during biasing. It is thus possible that there are much higher densities of nucleation sites initially, but competition for surface carbon amplifies growth of larger nuclei.

A higher density of nuclei leads to coalescence of grains at an earlier stage of the growth process, and we have considerable evidence that continuous diamond film formation can occur after only a few minutes of growth. The subsequent films are more highly-oriented since spatial correlations decay exponentially with distance and annihilation of interfacial defects is therefore more probable. However, for large area films, one must insure that the substrates are free of surface scratches, particulates, and pinholes that may compromise overall crystal quality.
Our discovery that A-plane sapphire can be used to grow (001) diamond promises to lead to improvements in diamond heteroepitaxy. We have observed that SrTiO$_3$ substrate quality is problematic, frequently exhibiting voids and macroscopic growth-induced stress bands. At high temperatures it tends to react even with refractory metals and is readily reduced in vacuum. Sapphire, on the other hand, exhibits much greater mechanical and chemical stability at high temperatures and is available with remarkably good crystallographic quality. We expect that this improved substrate system will enable the growth of wafer-scale heteroepitaxial diamond films in the near future.

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