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Effect of diffusion length on the nucleation of chemical vapour deposition diamond

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Abstract

Atomic steps have been suggested as preferential sites for nucleation. However, evidence from recent experiments on diamond growth using faceted sapphire as well as reconstructed silicon substrates shows that atomic steps alone do not always enhance nucleation in the chemical vapour deposition environment. The comparison of the diffusion length of the nucleation precursors and the width of the terraces between the surface steps provides further insights into this nucleation mechanism.

Keywords: Chemical vapour deposition; Diamond; Diffusion length; Nucleation; Sapphire; Steps; Terraces

1. Introduction

Chemical vapour deposition (CVD) diamond is an attractive material for many technological applications such as wear-resistant coatings, heat sinks, chemical sensors, optical windows and flat panel displays. While the fabrication of this material has been intensely studied, the nucleation and growth mechanism remains inconclusive. Some studies have suggested that atomic steps are the preferential sites for diamond nucleation [1,2]. A high diamond nucleation density of $\sim 10^8$ cm^{-2} and a preferential location of diamond nuclei along the steps of multi-vicinal or 7×7 reconstructed silicon surface in the hot filament chemical vapour deposition (HFCVD) environment was observed in a recent study [2]. The nucleation enhancement was attributed by Arnault et al. [2] to the larger surface diffusion length of the nucleation precursors compared to the width of the terraces on the reconstructed silicon surface. The surface diffusion length, λ, is defined as the mean path of the nucleation precursors before reacting or desorbing. The surface diffusion length of the nucleation precursors is estimated to be $\sim$0.1–0.15 μm while the terraces on the reconstructed silicon surface have a width of $\sim$6 nm. Since λ is larger than the distance between two terraces the probability for the diffusing nucleation precursors to reach the edge of terrace is high. Nucleation and growth of diamond can then quickly start along the surface atomic steps.

It is interesting to note that the faceted sapphire surface provides an excellent opportunity to investigate the effect of diffusion length on the nucleation and growth of CVD diamond. Single crystal α-(0 0 0 1) sapphire has unique surface properties. Annealing it in air at high temperatures induces the formation of a faceted surface but unlike the 7×7 reconstructed silicon surface it is stable under atmospheric conditions for long periods. While the height of the atomic steps is similar, the typical distance between the terraces is much wider than that observed on the reconstructed silicon surface. This article demonstrates that no nucleation enhancement will occur for the case where λ is smaller than or comparable with the width of the terraces. Some of the results of our recent diamond growth experiments on the faceted sapphire substrate had been reported [3–4] before but the effect of the diffusion length of the nucleation precursors on diamond nucleation in these experiments had not been studied. For the sake of clarity, these experiments as well the previously unreported results of diamond growth on the mirror-polished as-received single crystal α-(0 0 0 1) sapphire substrates are described in this article.

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2. Sample preparation

Thin square slabs of epi-polished single crystal α-(0 0 0 1) sapphire measuring about $6 \times 6 \times 0.5$ mm were used as substrates in this work. Apart from scratches due to commercial polishing, the surface of the as-received sapphire substrate was featureless with a root-mean-square (rms) roughness of ~0.29 nm. The sapphire substrates were cleaned with acetone, methanol and ethanol in an ultrasonic bath. The substrates were then annealed in air at 1400 °C for 1 h in a controlled environment tube furnace to obtain the faceted surface.

After annealing, the faceted sapphire substrates were inserted into the HFCVD reactor. Diamond was deposited for various periods between 15 min and 4 h with 1 vol.% methane in hydrogen gas mixture at the filament and substrate temperatures of 2100 and 850 °C, respectively. Diamond was also deposited on mirror-polished as-received sapphire substrates for comparison. The formation of diamond and the nature of the substrate surface were investigated using Raman spectroscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM). The Raman spectra were excited by an argon ion laser at 514.5 nm while the AFM analyses were performed in the non-contact mode. The deposition parameters in this work were similar to those used by Arnault et al. [2] and would serve as a good basis to investigate the effect of the diffusion length on diamond nucleation and growth.

3. Results and discussion

Fig. 1a shows the AFM image of the annealed sapphire substrate surface with distinct steps separated by wide atomically smooth terraces. The terrace-and-step morphology is observed over the entire substrate surface and is not confined to certain regions only. The AFM analysis indicates that the height of the steps ranges from ~0.2 to ~3 nm while the distance between two terraces is typically 2 orders of magnitude above than that observed in the case of reconstructed silicon surface. The height profile in Fig. 1 (b) shows that the distance between two terraces on the particular area of analysis is ~400–500 nm. Terraces of similar widths have also been observed recently by Kurnosikov et al. [5] and Yoshimoto et al. [6]. Single crystal sapphire substrates are usually prepared commercially by cutting and polishing a particular surface orientation and thus a slight unavoidable geometrical misorientation often happens due to the cutting machinery precision. The formation of a terrace-and-step morphology upon annealing provides a means of lowering the overall surface energy of the system [6].

After 15 min of deposition, isolated diamond particles could be observed on the faceted sapphire surface [3]. An early onset of diamond formation suggests that there is no intermediate layer between the diamond particles and the underlying sapphire substrate. Further indication of the absence of an intermediate layer formation comes from

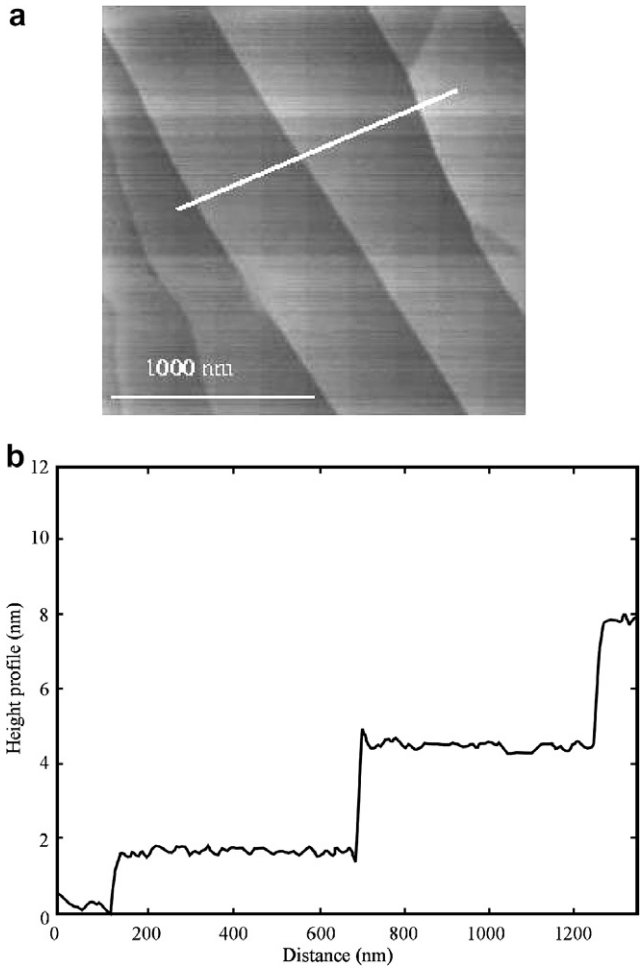

Fig. 1. (a) AFM image of the terrace-and-step structure induced by annealing in air. (b) Height profile of the faceted surface taken along the line indicated in (a) Ref. [4].

the AFM analysis, which reveals the pre-existing terrace-and-step morphology of the sapphire surface. An intermediate layer, if present, would cover pre-existing surface features, particularly if these features are of atomic height [7]. It is interesting to note that the atomic steps on the faceted sapphire surface are stable in the HFCVD environment long enough to act as preferential sites for diamond nucleation if any were to occur. Fig. 2 shows the faceted sapphire surface after 15 min in the HFCVD environment. The terrace-and-step morphology is still visible although there is some amount of erosion. The rms roughness is ~0.51 nm. The terrace-and-step morphology is, however, no longer discernable in surfaces that have been exposed to the HFCVD environment for longer periods. Instead, etch pits caused by atomic hydrogen could be seen on these surfaces. In spite of the initial presence of the atomic steps on the faceted surface of the sapphire substrate, no nucleation enhancement is observed. In addition, the nucleation density remains low despite longer deposition periods. The SEM analysis shows a scarce and uneven distribution of well-faceted diamond particles for all the deposition periods although a relatively good linear growth rate of