Lonsdaleite Diamond Growth on Reconstructed Si (100) by Hot-Filament Chemical Vapor Deposition (HFCVD)

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Abstract—In this paper, the growth of Lonsdaleite diamond using hot-filament chemical vapor deposition (HFCVD) on flashed and reconstructed Si (100) is reported. Surface morphology studies using scanning electron microscopy (SEM) show that the film is composed of decagonal and lonsdaleite-diamond particles. The X-ray diffraction (XRD) pattern has a strongest peak at 47° and a peak at 41°, which is indicative of Lonsdaleite nature of the grown diamond film. The Raman spectrum of the film shows a broadened diamond peak at wave number of 1,329 cm⁻¹, which has shifted towards the peak position corresponding to Lonsdaleite nature of the diamond (1,326 cm⁻¹).

Key words: Lonsdaleite, Diamond, HFCVD, Surface Reconstruction

INTRODUCTION

Since the determination of X-ray structure of the diamond, it has been known that the diamond is a tetrahedral network of carbon atoms and these atoms are arranged in a cubic lattice. Furthermore, it is also well known that there are two forms of diamond, i.e., the cubic diamond and the hexagonal diamond (also called Lonsdaleite). The Lonsdaleite diamond is found only in the bulk natural diamond. It has broad bands and is mostly observed in shock wave produced diamonds. The peaks in the Raman spectra are positioned in the wave number range from 1,315 to 1,326 cm⁻¹. In fact, various amorphous metastable and crystalline phases of carbon such as diamond, nano-tube, and fullerene like C₆₀ can exist; and most of them have been grown under non-equilibrium conditions [Spear and Dismukes, 1999]. Diamond is a metastable form of carbon compared to graphite at low pressure growth. The structure of graphite was formed by two-layer stacking sequences, ARAR of flat hexagonal (0001) carbon atomic planes, but diamond structure was formed by three-layer stacking sequences…ABCABCABC…of the same hexagonal, but puckered (111) carbon atomic planes. It has been reported that the Lonsdaleite diamond is detected in meteorites. Although Lonsdaleite was found in bulk diamonds of meteorites, it is not clear whether it exists in the CVD diamond by Lawrence and Kania, 1992. In thermal equilibrium conditions, the diamond phase is stable under a high temperature of about 2,300°C and a high pressure of about 40-50 Kbar. But under a normal chemical vapor deposition (CVD) growth conditions, i.e., under a low pressure of a few tens Torr, the nucleation and growth of diamonds can occur in non-equilibrium conditions, and hence the nucleation and growth will be controlled by kinetic laws rather than by thermodynamics. However, because of relatively large surface free energy of diamond and its small lattice constant compared to other semiconductors, diamond nucleation on semiconductor or non-diamond substrates is hardly achieved [Warzinger et al., 1996]. Therefore, various methods of nucleation enhancement, i.e., mechanical scratching (or grinding) and bias enhancement nucleation (BEN), surface carbonization, ion-implantation, use of carbon seeding layer etc. are used [Yogo et al., 1991; Stoner et al., 1993]. The property of CVD-diamond strongly depends on the nucleation enhancement method and the depositing parameters. Therefore, such flexibility of CVD techniques can enable us to produce the CVD diamond film with various structures, properties and qualities. To our knowledge, reports are not available for the growth of Lonsdaleite diamond except the work of Lee et al. [1998] reporting the growth of Lonsdaleite-like Carbon using HFCVD. In this paper, we report the evidence of the Lonsdaleite diamond grown by HFCVD on clean (flashed and reconstructed) Si (100) at specific deposition condition based on SEM, XRD and Raman spectroscopy results.

EXPERIMENT

Diamond films were deposited on Si (100)-2×1 surface using hot filament CVD technique. Prior to diamond growth, Si surface was flashed and reconstructed. The p-type Si (100) wafers of dimensions 13×7×0.5 mm were used as a substrate. For cleaning Si substrate, they were first degreased, then chemically etched by repeated oxidation and etching processes and finally protected by a thin oxide layer (using the so-called Shazzik method) [Isilzouk and Shashi, 1985]. The cleaned substrate was then transferred to the high-vacuum chamber (pressure of ~1×10⁻⁷ Torr) by using a specially designed substrate holder suitable for passing current to the substrate for flashing purpose. Thin oxide layer was removed by heating (known as flashing process) the substrate to 1,200°C in H₂ atmosphere (30 Torr pressure) until the oxygen species from the surface was completely removed. This was confirmed by X-ray photoelectron spectroscopy study (ESCALAB230, VG Microtech, UK) without exposing the substrate to ambient atmosphere. At the final flashing stage, the surface was reconstructed by slow cooling from 1,000°C to room temperature at the rate of 2°C/sec. The surface cleanliness was confirmed by XPS, and the surface reconstruction was confirmed by the two-fold 2×1 low electron energy dif-