

In-situ Incorporation of Lithium and Nitrogen into CVD Diamond Thin Films

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ABSTRACT

Experiments were performed to incorporate Li and N simultaneously into the diamond lattice during hot-filament chemical vapour deposition in an attempt to produce n-type semiconducting diamond with useful electronic characteristics. Microcrystalline diamond films were grown using a mixture of methane/ammonia/hydrogen gases with tantalum as the filament. The Li was added by placing crystals of lithium nitride (Li_3N) on the substrate and allowing them to melt and then slowly diffuse into the film. SIMS depth profiles showed that this process produced high levels of Li and N (0.05% - 0.5%) situated in the same region within the diamond film. The crystallinity and morphology of diamond crystals produced were confirmed using laser Raman spectrometry and scanning electron microscopy.

INTRODUCTION

Despite recent developments in doping diamond films with phosphorus, nitrogen, antimony, arsenic and sulfur, the production of n-type semiconducting diamond with good electronic properties remains elusive [1-4]. Lithiated diamond surfaces were suggested to produce low work-function materials [5, 6] and theoretical studies have predicted that interstitial lithium will act as a shallow donor and will enhance the electrical properties of diamond [7]. The energy to excite an electron from the lithium donor level to the conduction band of diamond is calculated to be less than 0.3 eV [8], however this has proved difficult to obtain experimentally. Research has been focused on trying to force Li into the diamond lattice by implantation, diffusion and insertion during growth, but in all cases the Li remained inactive inside the diamond lattice [9, 10]. This is partly due to the low solubility of Li, but also to its high mobility in diamond at high temperature which causes diffusion and aggregation of the Li into unwanted Li clusters [7]. It has been suggested [11] that this Li diffusion can be prevented by simultaneously adding nitrogen together with Li, with the N acting as a trap to pin down the Li in the diamond lattice and reduce its mobility. In theory, the electrons from an interstitial Li are transferred through a substitutional N atom directly into the diamond lattice. Thus, it is suggested that if a suitable co-doping process can create defect sites with 1:1 ratio of Li:N, this could produce n-type semiconducting diamond with a shallow donor level and high electron mobility.

In this paper, we present the results of a study to incorporate both Li and N while growing diamond thin films using hot-filament chemical vapour deposition (HFCVD) system. Secondary Ion Mass Spectrometry (SIMS) depth-profile analysis is presented to show the concentration of both dopants and the thickness of the dopant layer inside the diamond film.

EXPERIMENT

To grow lithium-nitrogen-codoped diamond, lithium nitride (Li_3N) and ammonia gas were used as lithium and nitrogen precursors, respectively.

Single-crystal Si wafers (100) were used as the substrate which were pre-treated by a manual abrasion technique using 1-3 μm diamond particles. Diamond was grown in a hot filament reactor using standard CVD conditions with the distance between the substrate and the tantalum filament fixed at 3 mm. The temperature of the substrate stage was then increased to approximately 400 $^\circ\text{C}$ using a heater. Undoped diamond was deposited using a standard ratio of 1% CH_4 in H_2 , and for N-doped diamond 0.38% of NH_3/H_2 was added to this mixture. The pressure of the chamber was set at 20 Torr. The filament temperature was measured using an optical pyrometer and kept between 2100 and 2250 K. These conditions fabricated diamond at a rate of $\sim 0.5 \mu\text{m h}^{-1}$.

For Li addition, a Li_3N suspension was prepared by dissolving 5 mg of polyoxyethylene ether in 5 ml of chloroform followed by the addition of 85 mg of Li_3N powder. The reddish-black mixture was sonicated for one hour in an ultrasonic bath. 200 μl of this Li_3N suspension was drop cast onto the surface of the diamond film and allowed to dry before being placed into the HFCVD reactor. The substrate was then heated by the filament (2100 K) in a pure H_2 atmosphere for an hour. This served to melt the Li_3N powder and to partially diffuse Li into the diamond surface. Care had to be taken not to overheat the surface or the liquid Li_3N would evaporate and be pumped away. Next, 1% $\text{CH}_4/0.38\% \text{NH}_3/\text{H}_2$ was flowed into the chamber for 15 minutes to initiate diamond growth and to encapsulate the Li within the newly growing diamond layer. After 5 h of growth (film thickness $\sim 3 \mu\text{m}$), the sample was cooled down under vacuum before being taken out in air.

To produce a completely encapsulated layer with high N and Li content, the deposition was performed in 3 stages. First an undoped diamond layer was deposited to a thickness of $\sim 2 \mu\text{m}$. Then an N-doped diamond layer was deposited to a thickness of $\sim 0.5 \mu\text{m}$. After that, the Li_3N procedure was performed to produce a Li-N-codoped layer of thickness $\sim 200 \text{ nm}$. Finally, this layer was embedded by depositing a capping layer of N-doped diamond $\sim 150 \text{ nm}$ thick.

The film morphology, quality and concentration of dopants were characterised using scanning electron microscopy (SEM), laser Raman spectrometry and secondary ion mass spectrometry (SIMS). The absolute concentrations of N and Li in the diamond were quantified using single-crystal diamond samples implanted with known concentrations of Li and N for use as SIMS calibration. The detection limit for Li and N in the instrument was $2.03 \times 10^{17} \text{ cm}^{-3}$ and $1.15 \times 10^{19} \text{ cm}^{-3}$, respectively.

DISCUSSION

Li-N-codoped diamond exhibited a typical Raman spectrum that was almost identical to undoped CVD diamond films grown with the same CH_4 content (see Figure 1). The diamond peak at 1332 cm^{-1} and graphitic G-band at $\sim 1580 \text{ cm}^{-1}$ are present, but no new peaks corresponding to N or Li are observed.

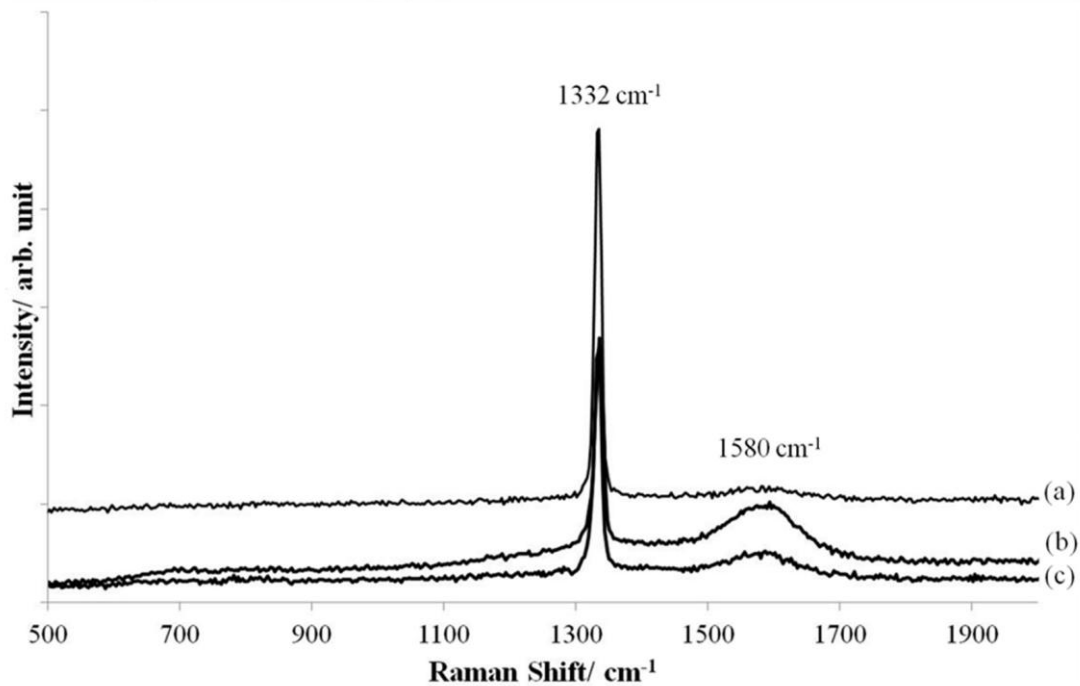


Figure 1: Raman spectrum (325 nm He-Cd laser excitation) obtained from (a) undoped diamond, (b) N-doped diamond and (c) Li-N-codoped diamond.

Figure 2 shows the morphology of the diamond thin films before and after the addition of lithium nitride. The undoped and N-doped diamond exhibited microcrystalline facets (Figure 2(a,b)). After addition of Li, the facets became much rougher, suggesting new nucleation sites had been created, possibly as a result of localised etching of the surface by Li [12] (Figure 2(c,d)). The etching and surface modification only occurred on the surface in a layer less than 100 nm in thickness (Figure 2(e)). Based on the micrographs and Raman spectra in Figure 1, we suggest that the Li etches the graphitic carbon at the grain boundaries of the diamond thin film. This might explain the reduction of the graphitic feature at 1580 cm^{-1} in Figure 1 suggesting the improvement in diamond quality due to the etching and re-nucleation of diamond surfaces.

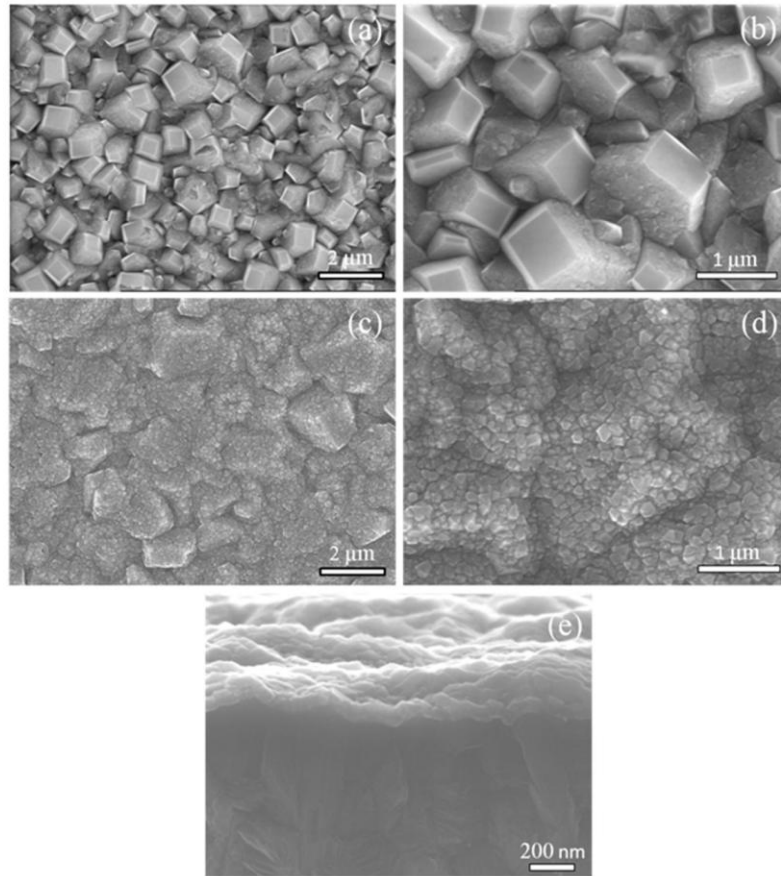


Figure 2: SEM micrographs showing the morphology of: (a) & (b) N-doped diamond, and (c), (d) & (e) Li- N-codoped diamond.

Figure 3 shows the SIMS depth-profile analysis of the Li-N-codoped diamond thin film. The Li signal was detected as Li^+ while the nitrogen signal was detected as CN^- . The Li signal is centred at a depth of ~ 200 nm beneath the diamond surface, with a spread of ~ 100 nm either side due to diffusion. The maximum concentration of Li detected was $5.02 \times 10^{19} \text{ cm}^{-3}$ and average of $3.73 \times 10^{21} \text{ cm}^{-3}$ was detected throughout the diffusion region. The N signal was detected only in the first 500 nm inside the diamond thin film, as expected. The maximum concentration of nitrogen atoms embedded in the film were $4.72 \times 10^{20} \text{ cm}^{-3}$ which is ~ 10 times more than the Li content. This overdoping with N had been done to ensure all that all the Li atoms inside the diamond film were adjacent to at least one N and so were immobilised within the diamond lattice.

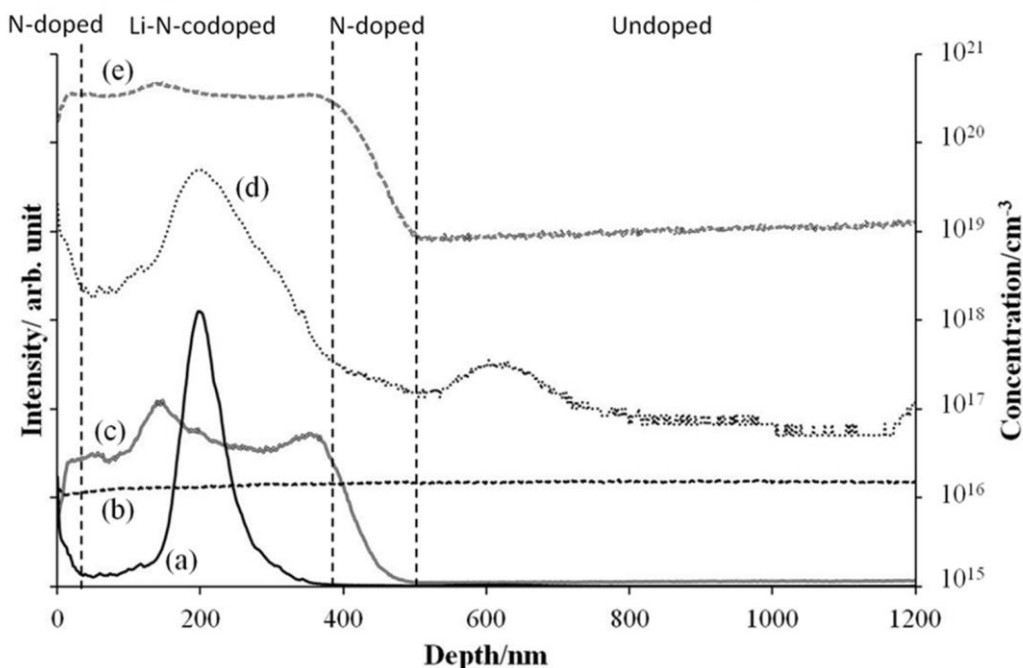


Figure 3: SIMS depth profile of the Li-N-codoped diamond thin film. Shown on the plot are the raw data for (a) Li, (b) C and (c) N (CN⁻) as intensity, as well as the absolute calibrated concentrations of (d) Li and (e) N, as a function of depth beneath the diamond surface.

The carbon signal remains constant for all the layers and serves as the baseline from which to calculate the concentrations of Li and N. It can be seen that the nanocrystalline N-doped diamond that grew on the outer surface (topmost 50 nm) still contains a considerable amount of Li. This may due to the high solubility of Li in sp² carbon structures compared to diamond [13].

CONCLUSIONS

Li-N-codoped diamond was synthesised by using Li₃N and ammonia gas as precursors. High amounts of Li (0.05%) and N (0.47%) were detected within the same region inside the diamond film, showing that this process is a successful method to incorporate these elements into diamond. The overall morphology of the diamond was not affected much by the incorporation of N, but Li caused some renucleation on the diamond surface possibly as a result of micro-etching of grain boundaries. The Raman spectra from the N- and Li-N-doped diamond show no significant differences from those of undoped diamond grown under the same CH₄ concentrations – suggesting that the film quality is not significantly affected by the presence of these impurities. The next stage of this work will be to perform electrical tests to determine whether the N and Li dopants are electrically active, and serve to impart n-type semiconductive behaviour, or are simply inert impurities.

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