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HAL Id: cea-03141091
https://hal-cea.archives-ouvertes.fr/cea-03141091
Submitted on 15 Feb 2021

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Cite as: Appl. Phys. Lett. 118, 061901 (2021); https://doi.org/10.1063/5.0033741
Submitted: 20 October 2020 . Accepted: 28 January 2021 . Published Online: 09 February 2021

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Note: This paper is part of the Special Topic on Ultrawide Bandgap Semiconductors.

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ABSTRACT
The growth of large-area diamond films with low dislocation density is a landmark in the fabrication of diamond-based power electronic devices or high-energy particle detectors. Here, we report the development of a growth strategy based on the use of micrometric laser-pierced hole arrays to reduce dislocation densities in heteroepitaxial chemical vapor deposition diamond. We show that, under optimal growth conditions, this strategy leads to a reduction in dislocation density by two orders of magnitude to reach an average value of \(6 \times 10^5\) cm\(^{-2}\) in the region where lateral growth occurred, which is equivalent to that typically measured for commercial type Ib single crystal diamonds.

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Due to its exceptional chemical/physical properties, such as a wide bandgap energy, high breakdown electric field, high carrier mobility, high thermal conductivity, and low dielectric constant, Chemically Vapor Deposited (CVD) diamond is a promising material for applications in power electronic devices and particle detectors. Nevertheless, the manufacturing of diamond devices is still hampered by the mm\(^2\) size and the number of extended defects present in the available single crystal substrates. To overcome these issues, several approaches were recently developed. For example, the growth of a wafer larger than 1 in. of single crystal diamond using the mosaic production method was reported. However, the area close to the junction between the initial substrates remained defective, thus limiting the use of this material in electronic or optical applications. Heteroepitaxial growth of diamond on Ir/MgO (100), Ir/YSZ/Si (001) [Iridium/Yttria-Stabilized-Zirconia/Silicon(001)], and Ir/SrTiO\(_3\)/Si (001) substrates was also developed, leading to sizes of up to several inches. However, the crystalline quality lacked significantly behind that obtained for homoepitaxial films because of the difference in the lattice parameter between Ir and diamond (7.2%). This indeed led to strain (~0.68 GPa) and high threading dislocation densities typically in the range of \(10^5\)–\(10^6\) cm\(^{-2}\) for thicknesses of a few hundreds of \(\mu\)m. On the contrary, synthetic commercial type Ib High Pressure High Temperature (HPHT) diamonds only exhibit densities of \(10^4\)–\(10^5\) cm\(^{-2}\) after 1-mm-thick heteroepitaxial film growth. Tang et al. reported a reduction in dislocation densities to \(10^4\) cm\(^{-2}\) after 1-mm-thick heteroepitaxial film growth. Ichikawa et al. demonstrated the fabrication of heteroepitaxial diamond with high crystalline quality using grid patterned nucleation and growth on Ir with a dislocation density of \(9 \times 10^5\) cm\(^{-2}\).

More recently, Ohmagari et al. developed an original approach taking advantage of tungsten metal impurities incorporation during
diamond growth performed by hot-filament CVD, which can reach concentrations as high as $10^{16}$–$10^{19}$ cm$^{-3}$. The presence of these metallic impurities induced localized internal stress that interacted with dislocations and strongly influenced their propagation and, thus, their density. This technique was applied to heteroepitaxial diamond, leading to a reduction in dislocation density although no quantitative value was reported. A high concentration of metallic impurity contamination still necessarily remains though, which is not always acceptable for electronic applications.

Despite those effort and improvements, dislocation density remains fairly high in heteroepitaxial diamond films. Moreover, most of the actual strategies require tedious fabrication steps: growth of mm-thick layers or time-consuming cleanroom processing to produce patterned structures. Even if these techniques are quite well developed and used for the production of single crystal substrates of semiconductor material such as GaN, only a few examples of attempts have been made to apply these strategies to heteroepitaxial diamond.

In this work, a strategy aiming at reducing dislocation density in heteroepitaxial diamond is proposed. It builds on a previous work from our group using a pierced HPHT single crystal substrate, which led to homoepitaxial CVD diamond films with the dislocation density as low as $10^2$ cm$^{-2}$. To transfer this concept to heteroepitaxial wafers, a $6 \times 6$ array of $500 \times 500 \mu m^2$ holes was laser-pierced before performing the growth of several hundreds of micrometer-thick CVD diamond to fill up the holes.

Two commercial heteroepitaxial diamond substrates ($10 \times 10 \times 0.7 \text{ mm}^3$) were used (named A1 and A2). They were supplied by the German spin-off company Augsburg Diamond Technology GmbH, and both substrates have lateral and top faces oriented along the (100) directions. They were presumably grown on an Ir/YSZ template by the German spin-off company Augsburg Diamond Technology GmbH, and used for the production of single crystal substrates of semiconductor material such as GaN. Only a few examples of attempts have been made to apply these strategies to heteroepitaxial diamond.

Temperature (°C) 860 860
Duration (h) 140 68
Thickness (μm) 600 300

TABLE I. Growth conditions used for the overgrowth step.

In crystalline quality was found. Indeed, the corresponding Full Width at Half Maximum (FWHM) of the diamond peak for side 1 was narrower than that on side 2 (3.11 cm$^{-1}$ vs 4.78 cm$^{-1}$). This is possibly related to the growth direction of the sample. In fact, Stehl et al. showed that crystalline quality improves with the layer thickness. This would indicate that side 1 is the growth (i.e., thickened) side, while side 2 is presumably the diamond/iridium nucleation side. To be in optimal conditions, we selected the side with the lowest FWHM to perform the overgrowth step. A thick diamond layer was then deposited on samples A1 and A2 using a home-made CVD reactor under previously optimized growth conditions as reported in Table I.

After 140 h of growth, a 600-μm-thick layer of CVD diamond was obtained on A1. The hole array fully disappeared with the square holes progressively reducing in size, indicating that growth proceeded along (100) directions. This corresponds to a normal growth rate.
(GrN) of 4.3 μm/h. The hole array was filled up after 113 h, and the lateral growth rate (Grlat) was then estimated to be 2.5 μm/h. The growth rate ratio is calculated according to the below formula:

$$\frac{Gr_{\text{lat}}}{Gr_N} = \frac{\frac{1}{2}}{\frac{I}{T_s}},$$

with \(l\) being the hole’s length (500 μm), \(t_f\) the time needed to fill up the holes, \(e\) the thickness of the grown layer, and \(t_g\) the growth time. We obtain a ratio of 0.51.

The surface morphology [cf. Figs. 2(b) and 2(c)] is smooth as for homoepitaxial diamond films with a comparable thickness. The FWHM of the diamond Raman peak is 2.24 cm\(^{-1}\) on the area above the holes (where lateral growth occurred) and 2.3 cm\(^{-1}\) outside the hole area. These values are close to those measured for high-quality homoepitaxial single crystalline diamond\(^{40}\) and already suggest a significant improvement as compared to the initial heteroepitaxial substrate. We attribute this improvement to the thickening of the film under well-adapted growth conditions and high purity.

H\(_2\)/O\(_2\) plasma etching was carried out to reveal EP, but, as presented in Figs. 2(d) and 2(e), no specific difference between the area above and between the holes is evidenced, suggesting that dislocation density remained similar over the entire sample or even slightly higher in the laterally grown regions. Indeed, we estimated the EP density to be \(4.5 \times 10^7\) cm\(^{-2}\) between the holes and \(6 \times 10^7\) cm\(^{-2}\) in the laterally grown areas (above the holes). Thus, in contrast to our expectation, no reduction in dislocation density was observed on this sample as compared to the initial substrate. Nevertheless, in these growth conditions, we should emphasize that unlike in the previous work on single crystal growth over a pierced HPHT single crystal substrate,\(^{36}\) the lateral to normal growth rate ratio (Grlat/GrN) was inferior to 1. With such a small enlargement factor, we expect that the force exerted to bend dislocations toward the edges would not be high enough to prevent their vertical propagation along the \(\langle 001\rangle\) direction rather than in the lateral direction in order to minimize their energy.\(^{41}\) We, thus, repeated the overgrowth under different growth conditions, leading to an increased Grlat/GrN ratio.

To do so, we overgrew sample A2 with a methane percentage of 4% instead of 5% in the gas phase, which is well known to strongly affect the growth rate along the different crystallographic directions.\(^{42}\) In particular, the growth rate in the \(\langle 100\rangle\) direction is expected to decrease, thus inhibiting the growth of competitive faces and allowing a faster filling of the hole. The deposition duration was 68 h corresponding to a 300-μm-thick layer (i.e., a normal growth rate of 4.4 μm/h), and the hole arrays were filled up after 43 h, which corresponds to a lateral growth rate of 5.7 μm/h. Figures 3(a)–3(c) confirm the expected improvement in terms of lateral growth. The Grlat/GrN ratio with this improved set of parameters was, thus, estimated to be 1.35. In addition, the hole array could be filled up in a much shorter time. The narrow window of operating conditions should be highlighted here since such a small variation in the methane concentration was able to drastically change the enlargement of the hole.

In contrast to the first sample, after H\(_2\)/O\(_2\) plasma etching [cf. Figs. 3(d) and 3(e)], a significant difference in EP density between the areas above and between the holes was evidenced. A value of only \(6 \times 10^6\) cm\(^{-2}\) was estimated locally in the laterally grown region (i.e., above the holes), which is the lowest reported so far on a heteroepitaxial diamond film. A dislocation density of \(5 \times 10^6\) cm\(^{-2}\) was also measured outside the holes’ region. If we normalize to the entire surface of the sample, we reach an average density of \(4.6 \times 10^8\) cm\(^{-2}\), which is an order of magnitude better than the initial substrate before overgrowth but only moderately improved with respect to an untreated region. In fact, the surface covered by the holes currently represents only a modest 10% of the total area. By repeating the process with holes pierced in complementary areas, this averaged dislocation density value could be further improved. Moreover, we should emphasize that electronic devices fabricated on this large diamond platform could benefit from a lower dislocation density by being preferentially placed over the treated areas.

To further elucidate the growth mechanisms on the two overgrown samples, a thin cross-sectional slice was laser cut parallel to the \(\langle 100\rangle\) lateral face in the center of a hole line and polished. The slices were then observed using a DiamondView\textsuperscript{TM} that uses short-wavelength UV-light to excite fluorescence of the crystal (cf. Fig. 4).
On the PL image, the initial substrate exhibits a bright red color that masks any other possible luminescence. It is indicative of the presence of nitrogen-vacancy (NV) centers incorporated from nitrogen addition that was presumably used during growth by the supplier. On the contrary, the CVD overgrown films do not show the presence of impurities, but blue luminescence related to stress (A band). Interestingly, by comparing the cross sections of A1 and A2, we confirm that, when the methane percentage is reduced, the lateral growth rate is increased, leading to sharp holes with smaller aspect ratios. This type of geometry is favorable to the bending of dislocations horizontally so that they will end on the free surfaces of the disappearing holes as schematically shown in Figs. 4(c) and 4(d). This strongly supports the observed reduction in dislocation density by controlling their propagation direction. It relies on fine-tuning the hole’s aspect ratio during growth so that dislocations are bent and can no longer propagate vertically toward the surface. We produced heteroepitaxial diamond films with a density as low as $6 \times 10^5$ cm$^{-2}$ locally, in the region where lateral growth occurred, which is the lowest reported so far. This growth strategy, as long as the $\frac{Gr_{lat}}{Gr_N}$ ratio is greater than 1, paves the way for the production of large CVD diamond substrates having crystalline quality close to conventional mm$^2$ synthetic diamonds. By extending this technique and applying additional and complementary hole arrays, one can expect producing heteroepitaxial diamonds with unprecedented crystalline quality, which could serve as large-area wafers for power electronics. A multi-step process with holes pierced in different regions in each step can be

\[ \frac{Gr_{lat}}{Gr_N} < 1 \]

\[ \frac{Gr_{lat}}{Gr_N} > 1 \]
implemented to improve the ratio of the surface area treated to the total surface area of the samples and further decrease the average dislocation density.

This work was financially supported by ANR (Agence Nationale de la Recherche) and DGA (Direction Générale de l’Armement) through National Project DIAMWAFEL No. ANR-15-CE08-0034-03. ANR and CGI (Commissariat Générale à l’Investissement) are also gratefully acknowledged for their financial support through Labex SEAM (Science and Engineering for Advanced Materials and devices), Nos. ANR-10-LABX-0096 and ANR-18-IDEX-0001, and the Ile-de-France Region for their support within the framework of DIM SIRTEQ.

DATA AVAILABILITY

The data that support the findings of this study are available within this article.

REFERENCES


