PROPERTIES OF THICK HOMOEPITAXIAL DIAMOND LAYERS

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ABSTRACT

Single crystal diamond layers were grown epitaxially on natural diamond substrates using microwave plasma CVD deposition techniques. Epitaxial layers of up to 0.8mm in thickness were grown without macroscopic inclusions and cracks. X-ray analysis of both the substrate before growth and the epilayer substrate laminate suggest the major crystallographic defects of the epilayers to be dislocations growing out of the substrate.

INTRODUCTION

Diamond semiconductor electronic applications depend critically on the ability to grow low-defect, high-quality, single crystal diamond substrates. While most of the potential applications of diamond require a versatile range of both n-type and p-type dopants, most documented dopant behavior is restricted to nitrogen and boron found in naturally occurring diamond and hydrogen found routinely in CVD diamond(1,2,3). The development of processes and equipment for the routine deposition of single crystal chemical vapor deposited (CVD) diamond has allowed the development of processes for the controlled incorporation of dopants into these films. The properties of dopants in CVD diamond are closely linked to the evolution of diamond film quality. Homoepitaxial diamond single crystals grown using CVD techniques offer the opportunity to achieve the highest quality possible with this technology. Devices fabricated from homoepitaxial diamond should exceed the performance of comparable gemstone diamond devices if the proper process techniques are used to grow high quality single crystals.

EXPERIMENTAL

Homoepitaxial single crystal diamond layers were grown on naturally occurring type Ia and type IIa gemstone diamond substrates using microwave plasma assisted CVD deposition techniques. The substrates, purchased from Dubbledee-Harris, were polished and aligned with a (100) orientation. The reactor was a

microwave plasma assisted CVD diamond growth system employing a 2.45GHz power source. The reactor was equipped with gas sources and flow controllers for argon, hydrogen, methane, oxygen, carbon monoxide, phosphine and diborane. The gemstone diamond substrates were solvent degreased before growth and loaded into the reactor on silicon holders. The holder temperature was monitored by an optical pyrometer which indicated nominal growth temperatures of 800°C. Significant temperature variations could exist due to the proximity of the substrate to the plasma. The epitaxial layers grown ranged in thickness from 0.5μm to 800μm. The single crystal layers were grown both unintentionally doped and intentionally doped by means of gas phase introduction of diborane or phosphine gas. The homoepitaxial layers were analyzed by Raman spectroscopy, optical absorption spectroscopy, X-ray topography, X-Ray diffractrometry, and scanning electron microscopy.

Single crystals were grown both unintentionally doped and intentionally doped by means of gas phase introduction of diborane, phosphine and nitrogen gas. Thick epitaxial single crystals have significant advantages over thinner submicron layers with respect to the repeatable growth of low defect layers. The primary "killer defect" in single crystal diamond growth has been found to be the nucleation and growth of polycrystalline inclusions. Figure 1 shows a scanning electron micrograph of a 260μm thick epitaxial layer grown on top of a type IIa gemstone diamond of dimensions 4mm x 4mm x 250μm. Polycrystalline inclusions when present in thick layers are easily detected and rejected early in the device process flow allowing for much lower defect devices to be constructed. Figure 2 shows an 800 micron thick epilayer with no inclusions of the diamond face but with inclusions present on the diamond edges. Figures 3 and 4 show the respective optical micrographs of these two epilayers clearly delineating the defect free zones. As the inclusions are of the same dimension as the film thickness, they are very difficult to detect in thin submicron epilayers.

Another distinct advantage of thick epitaxial layers is it allows for characterization of the crystals with ultraviolet optical absorption techniques. A broad absorption merged with the band edge occurs in all the epilayers but due to the overall low absorption is only readily detected in the thicker and/or highly defective samples. This absorption shows up in the visible as a slight yellow-brown coloration and is not present in the type IIa substrates as received. Raman spectra and angle resolved Raman spectra, from some of the epilayer samples, show well defined shifts indicative of stress(4). This absorption may also arise from stress in the grown layers(5). The homoepitaxial layers were also analyzed by X-ray topography and diffractometry and the results compared with the device behavior. Select substrates were also analyzed prior to growth. Figs. 6 and 7 are diffractometer traces of two as received diamond substrates with FWHM peak widths of 180 and 240 arcseconds. These peak widths are typical of deformed, high dislocation density single crystals. These broad peak widths result in poor quality, low resolution x-ray topographs. Figure 8 is the diffractometer trace of the epilayer substrate laminate pictured in Fig. 1 showing a FWHM peak width of 180 arcseconds. The peak width of the homoepitaxial layer strongly suggests that it is the substrate limiting the perfection of the epilayers. Due to the high deformation of the substrate, dislocations are most likely the main crystallographic defect transmitted to the epilayer.

Planar photoconductive diodes were fabricated from the nominally undoped crystal layers. The photoconductive diode response was measured using pulsed ultraviolet laser light and the output signals were analyzed to derive the carrier mobility and lifetime. Table I lists the results for doped and undoped epilayers, polycrystalline diamond and type IIa natural diamond. Table I shows that both the undoped epitaxial and polycrystalline devices have similar performance to ones fabricated from type IIa crystals whereas doped layers result in poor performance. These results suggest that photoconductor mobility and lifetime are very sensitive to chemical purity and very insensitive to crystalline perfection.

Table I. Mobility and lifetime of single crystal diamonds

Dopant (type)	Gas Phase Concentration and Species	Photocarrier lifetime (ps)	Combined mobility $(cm^2/V\text{-}s)$
undoped (epi)	-	220	3500
phosphorus (epi)	0.9ppm phosphine	85	500
boron (epi)	0.9ppm diborane	90	200
undoped (type IIa nat.)	-	300	4000
undoped (poly)	-	100	4000

CONCLUSIONS

Thick homoepitaxial layers were grown and fabricated into photoconductor devices. The best high purity epitaxial layers had similar electronic performance to type IIa gemstones but also high purity polycrystalline layers. X-ray analysis suggests that the gemstone substrate perfection is limiting the performance of the epitaxial layers.

ACKNOWLEDGMENTS

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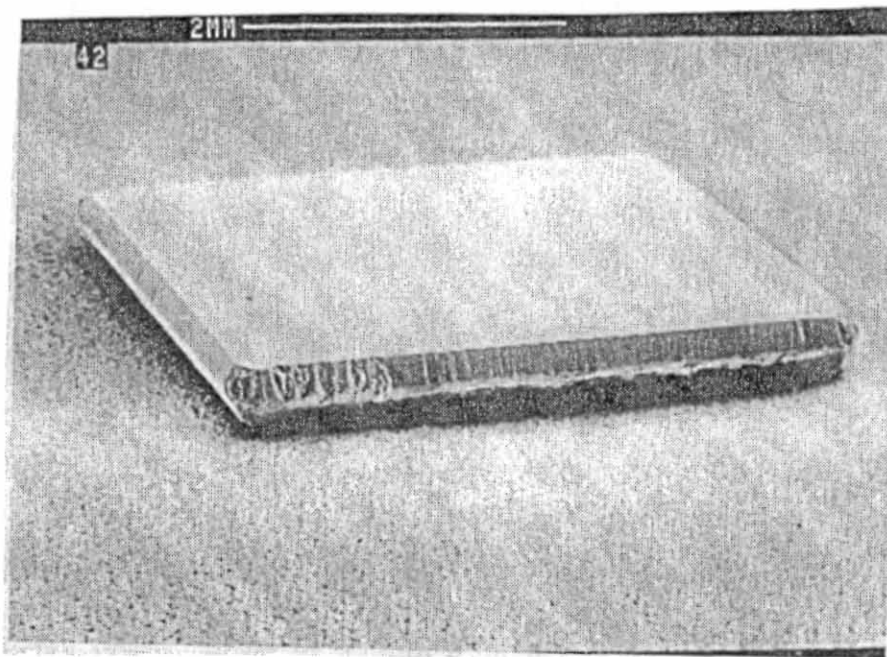5. J. Wilks and E. Wilks, *Properties and Applications of Diamond,* (Butterworth-Heineman, 1991), p.82

Figure 1. Scanning electron micrograph of a 260µm thick epitaxial layer grown on top of a type IIa gemstone diamond of dimensions 4mm x 4mm x 250µm.
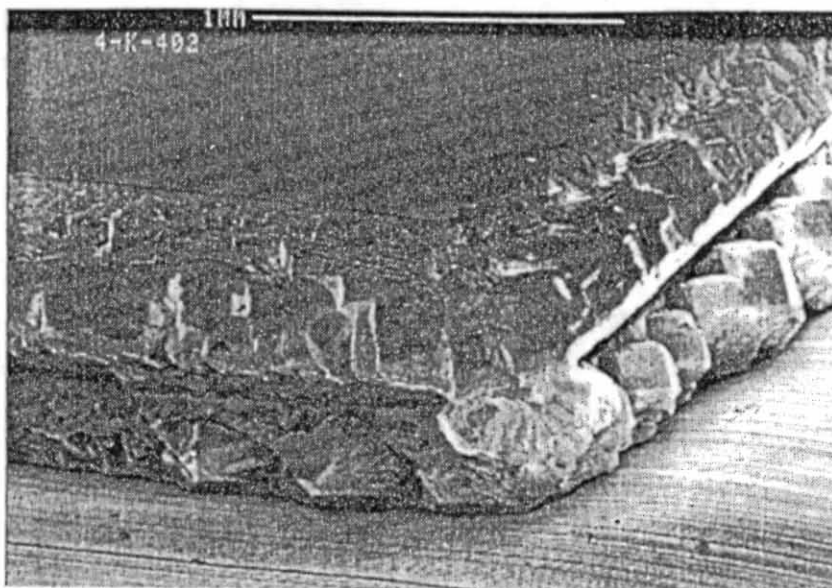

Figure 2. Scanning electron micrograph of a 800µm thick epitaxial layer grown on top of a type IIa gemstone diamond of dimensions 2mm x 2mm x 250µm.
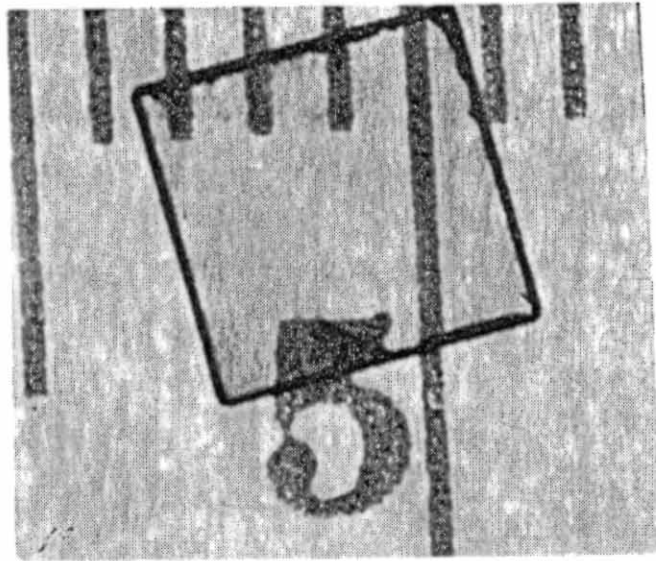
Figure 3. Optical micrograph of a 260 micron thick diamond epitaxial layer grown on top of a 4x4mm type IIa diamond 250 micron in thickness.
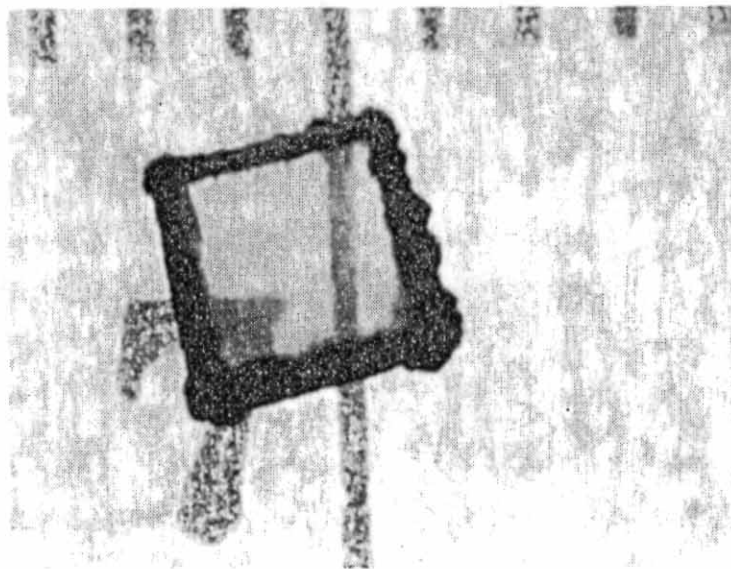

Figure 4. Optical micrograph of a 800 micron thick diamond epitaxial layer grown on top of a 4x4mm type IIa diamond 250 micron in thickness.
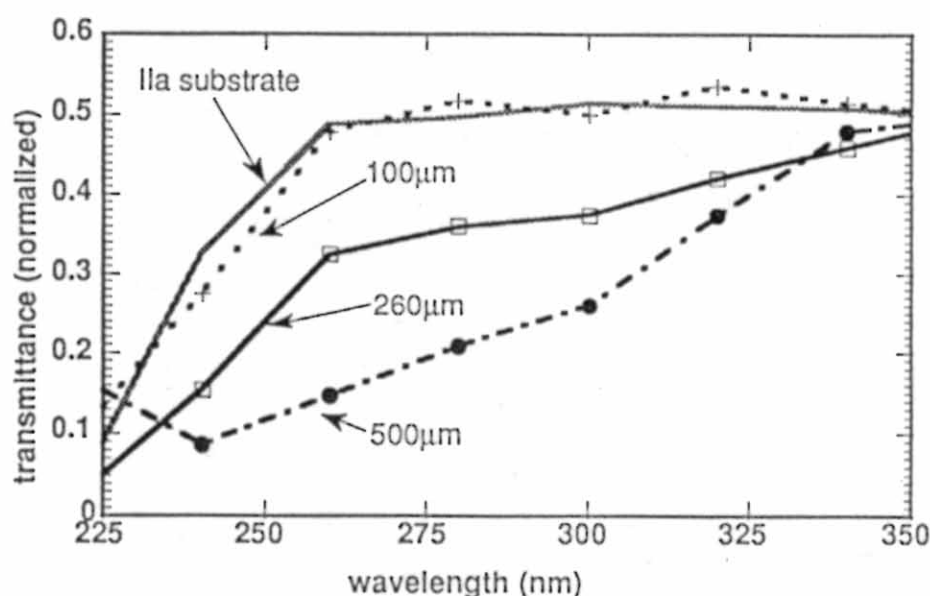
Figure 5. Ultraviolet transmission near the band edge of a gemstone type IIa diamond 250μm in thickness plotted along transmission curves for diamond epitaxial layers of thicknesses 100, 260, and 500μm. The epitaxial layers were deposited on type IIa diamond 250μm in thickness.
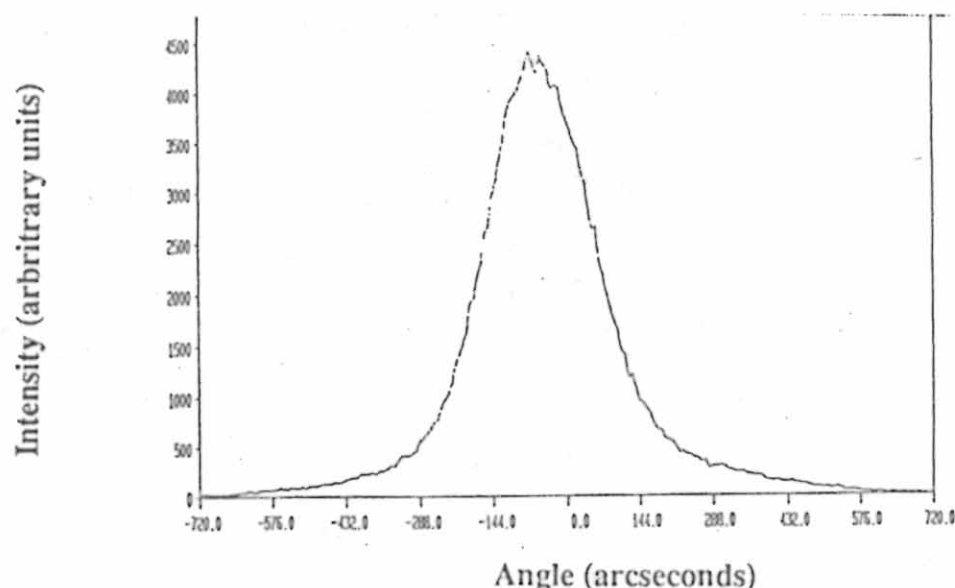

Figure 6. X-ray diffraction measurement of the (004) reflection peak, using CuKα_1 radiation, of a 2mm diameter by 250 microns thick type IIa substrate. The FWHM peak width is 240 arcseconds. There is no epilayer growth and the measurement was performed on the as received sample.
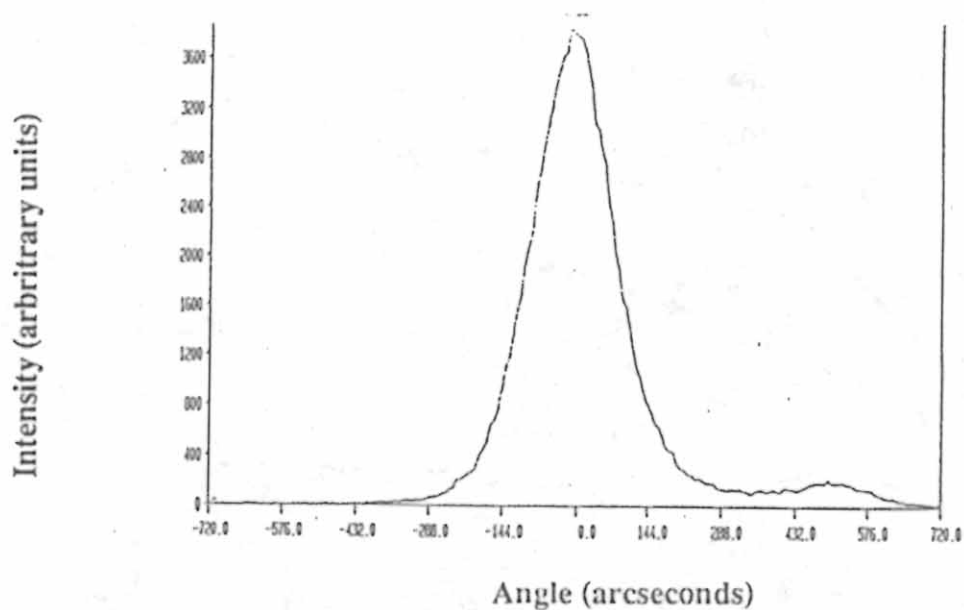
Figure 7. X-ray diffraction measurement of the (004) reflection peak, using CuKα1 radiation, of a 4mm by 4mm by 250 microns thick type IIa substrate. The FWHM peak width is 180 arcseconds. There is no epilayer growth and the measurement was performed on the as received sample.
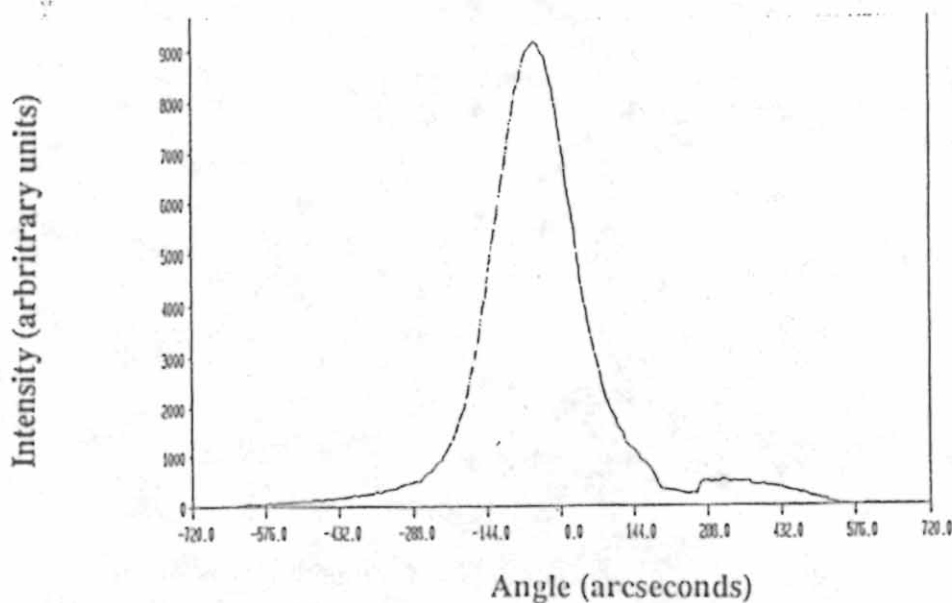

Figure 8. X-ray diffraction measurement of the (004) reflection peak, using CuKα1 radiation, of a 4mm by 4mm by 260 microns thick CVD diamond epilayer grown on top of a 4mm by 4mm by 250 microns thick type IIa substrate. The FWHM peak width is 180 arcseconds.