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Major Goals: We have achieved a “proof of concept” for n- and p-doping of diamond based on the recently discovered direct conversion of amorphous carbon into diamond at ambient temperatures and pressures in air. The key advantage stems from the novel growth approach, where the carbon layers are melted by using high-power nanosecond pulsed lasers in a highly super undercooled state, and then quenched rapidly either into a new state of carbon (Q-carbon) or into the single-crystal diamond phase in the presence of a template for diamond growth. Accordingly, it is envisioned that dopant impurities present in the amorphous carbon films can be incorporated into substitutional (electrically active) sites of diamond during rapid liquid-phase crystallization via the phenomenon of solute trapping. As this is a fundamentally nonequilibrium process, we have shown that dopant concentrations in electrically active sites for both n- and p-types to far exceed the thermodynamic equilibrium solubility limits, while maintaining the energy levels, overcoming the long-standing challenge of diamond. Feasibility studies on n-type doping (N dopants) and p-type doping (B dopants) have been demonstrated by incorporating these dopants into carbon by ion implantation for N and laser evaporation for B. After laser annealing with single laser pulse (ArF laser, energy density = 0.65 Jcm-2, pulse duration 20ns, and laser photon energy 6.0 eV at 193nm), we obtained doped diamond after recrystallization. Lattice location (substitutional versus interstitial) studies were performed by using atomic resolution (STEM-Z) techniques and the results correlated with electrical activation and carrier transport measurements. These results were found to be consistent with our earlier work in silicon, we showed that this technique can be used to far exceed thermodynamic solubility limits via solute trapping. During solute trapping, dopants are buried against their chemical potential as result of strong barriers providing traps. Preliminary investigations are underway to fabricate diamond p-n junction diodes and investigate their characteristics for next-generation diamond electronics.

Accomplishments: In this method, carbon thin films are deposited on a substrate such as sapphire, silicon, glass and even heat-sensitive polymer substrate. The thickness of carbon films is varied from 50-500nm. The as-deposited is characterized by Raman spectroscopy to determine SP3 to SP2 ratio. These films are doped with nitrogen by two methods: (1) by adjusting the nitrogen partial pressure (5.0x10-3, 5.0x10-2, 5.0x10-1 Torr); and (2) by bombarding simultaneously with N2+ (0.5-1.0 KeV) during carbon thin film deposition. The doping with boron is achieved by co-evaporation of B and C. The nitrogen concentration is adjusted by controlling the nitrogen partial pressure and by measuring the nitrogen ion flux. Subsequently, these films are irradiated with high-power nanosecond pulses with energy density 0.5-1.0Jcm-2, pulse duration 20-40 nanoseconds, and laser wavelength for ArF Excimer laser of 193nm. The carbon film is melted in the highly super undercooled state and quenched within 200-250 nanoseconds. By controlling the quenching from the liquid, we can nucleate diamonds in the form of nanodiamonds (2-8nm), microdiamonds (100-1000nm), and large-area thin films. By providing single-crystal substrate template, we are able grow epitaxial single-crystal large-area thin films. The nitrogen is incorporated into diamond during rapid liquid-phase growth, where dopant concentrations can far exceed the thermodynamic solubility limits. The number density of NV defects can be controlled by the nitrogen concentrations in the as-deposited films. The concentration of other dopants can also be introduced during carbon thin film deposition. These films are characterized by high-resolution scanning electron microscopy, electron energy loss spectroscopy, electron backscattered diffraction (EBSD) with characteristic diamond Kikuchi patterns, X-ray diffraction, X-ray photoelectron spectroscopy (XPS), photoluminescence (325nm source) and Raman spectroscopy (source 633nm).

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Results Dissemination: 1. J. Narayan and A. Bhaumik, APL Materials, 4, 020701 (2016).
2. A. Bhaumik, R. Sachan, J. Narayan; J. Appl. Phys. 122, 045301 (2017).

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NAI (LIFE FELLOW)

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Person Months Worked: 6.00 **Funding Support:**
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International Travel:
National Academy Member: N
Other Collaborators:

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Doping of Diamond beyond Thermodynamic Solubility Limit for Electronic Applications

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Doping of Diamond beyond Thermodynamic Solubility Limit for Electronic Applications, J. Narayan, NC State PI (ARO W911NF-16-1-0375)

We have achieved a “proof of concept” for n- and p-doping of diamond based on the recently discovered direct conversion of amorphous carbon into diamond at ambient temperatures and pressures in air. The key advantage stems from the novel growth approach, where the carbon layers are melted by using high-power nanosecond pulsed lasers in a highly super undercooled state, and then quenched rapidly either into a new state of carbon (Q-carbon) or into the single-crystal diamond phase in the presence of a template for diamond growth. Accordingly, it is envisioned that dopant impurities present in the amorphous carbon films can be incorporated into substitutional (electrically active) sites of diamond during rapid liquid-phase crystallization via the phenomenon of solute trapping. As this is a fundamentally nonequilibrium process, we have shown that dopant concentrations in electrically active sites for both n- and p-types to far exceed the thermodynamic equilibrium solubility limits, while maintaining the energy levels, overcoming the long-standing challenge of diamond. Feasibility studies on n-type doping (N dopants) and p-type doping (B dopants) have been demonstrated by incorporating these dopants into carbon by ion implantation for N and laser evaporation for B. After laser annealing with single laser pulse (ArF laser, energy density = 0.65 Jcm^{-2}, pulse duration 20ns, and laser photon energy 6.0 eV at 193nm), we obtained doped diamond after recrystallization. Lattice location (substitutional versus interstitial) studies were performed by using atomic resolution (STEM-Z) techniques and the results correlated with electrical activation and carrier transport measurements. These results were found to be consistent with our earlier work in silicon, we showed that this technique can be used to far exceed thermodynamic solubility limits via solute trapping. During solute trapping, dopants are buried against their chemical potential as result of strong barriers providing traps. Preliminary investigations are underway to fabricate diamond p-n junction diodes and investigate their characteristics for next-generation diamond electronics.

Introduction:

Diamond and c-BN have unparalleled physical and chemical properties, including record thermal conductivity, high band gaps (5-52 eV for diamond and 6.40eV for c-BN), extremely high breakdown fields, high electrical resistivity when undoped, semiconductor when doped, high carrier mobilities, and negative electron affinity with efficient field emission. These properties lead to very high Johnson figure of merit of 8200 (relevant for high-power and high-temperature devices) and Keyes figure of merit of 32 (relevant for integrated circuits) compared to 1 for silicon [1-5]. The realization of these diamond and c-BN based devices requires efficient p- and n-type doping [6]. While p-type doping of diamond using boron has shown some success, the n-type doping has been quite problematic, resulting in poor mobilities and unreliable dopant efficiency. The primary objective of this proposal is to develop a novel approach for doping diamond with n- and p-type dopants through Q-carbon (melting and quenching), while utilizing the phenomenon of solute trapping [7].

Experimental Details:

In this method, carbon thin films are deposited on a substrate such as sapphire, silicon, glass and even heat-sensitive polymer substrate. The thickness of carbon films is varied from 50-500nm. The as-deposited is characterized by Raman spectroscopy to determine SP^3 to SP^2 ratio. These films are doped with nitrogen by two methods: (1) by adjusting the nitrogen partial pressure ($5.0x10^{-3}$, $5.0x10^{-2}$, $5.0x10^{-1}$ Torr); and (2) by bombarding simultaneously with N_2^+ (0.5-1.0 KeV) during carbon thin film deposition. The doping with boron is achieved by co-evaporation of B and C. The nitrogen concentration is adjusted by controlling the nitrogen partial pressure and by measuring the nitrogen ion flux. Subsequently, these films are irradiated with high-power nanosecond pulses with energy density $0.5\text{-}1.0Jcm^{-2}$, pulse duration 20-40 nanoseconds, and laser wavelength for ArF Excimer laser of 193nm. The carbon film is melted in the highly super undercooled state and quenched within 200-250 nanoseconds. By controlling the quenching from the liquid, we can nucleate diamonds in the form of nanodiamonds (2-8nm), microdiamonds (100-1000nm), and large-area thin films. By providing single-crystal substrate template, we are able grow epitaxial single-crystal large-area thin films. The nitrogen is incorporated into diamond during rapid liquid-phase growth, where dopant concentrations can far exceed the thermodynamic solubility limits. The number density of NV defects can be controlled by the nitrogen concentrations in the as-deposited films. The concentration of other dopants will also be introduced during carbon thin film deposition. These films are characterized by high-resolution scanning electron microscopy, electron energy loss spectroscopy, electron backscattered diffraction (EBSD) with characteristic diamond Kikuchi patterns, X-ray diffraction, X-ray photoelectron spectroscopy (XPS), photoluminescence (325nm source) and Raman spectroscopy (source 633nm).

Results:

Fig. 1 shows results on the direct conversion of carbon into nanodiamond, microdiamond, and large-area single crystal films after a single pulse of excimer laser irradiation (Pulse duration = 20ns, ArF wavelength = 193nm) of carbon films about 500nm thick. Nanodiamonds (2-8nm) are formed as a result of homogeneous nucleation from super undercooled melt, as shown in Fig 1 (a). As more time is allowed for growth, microdiamonds (average size 500nm) are formed, as shown in 1(b). By providing an epitaxial template, we are able to form large-area single-crystal films through the paradigm of domain matching epitaxy (DME). The DME paradigm entails the matching of integral multiples of lattice planes across the film-substrate interface. These films were also characterized by electron backscattered diffraction (EBSD), and the results showed characteristic diamond Kikuchi patterns (as shown in Fig. 1(c)). Fig. 2 shows Raman spectra using 633nm source from as-deposited carbon film containing D (1350 cm^{-1}) and G (1560 cm^{-1}) peaks. After a single laser pulse, a sharp peak at 1332 cm^{-1} is observed without the presence of other carbon phases, showing a compete conversion of carbon into diamond. Similar results are shown from another from a high-quality fully converted diamond film.

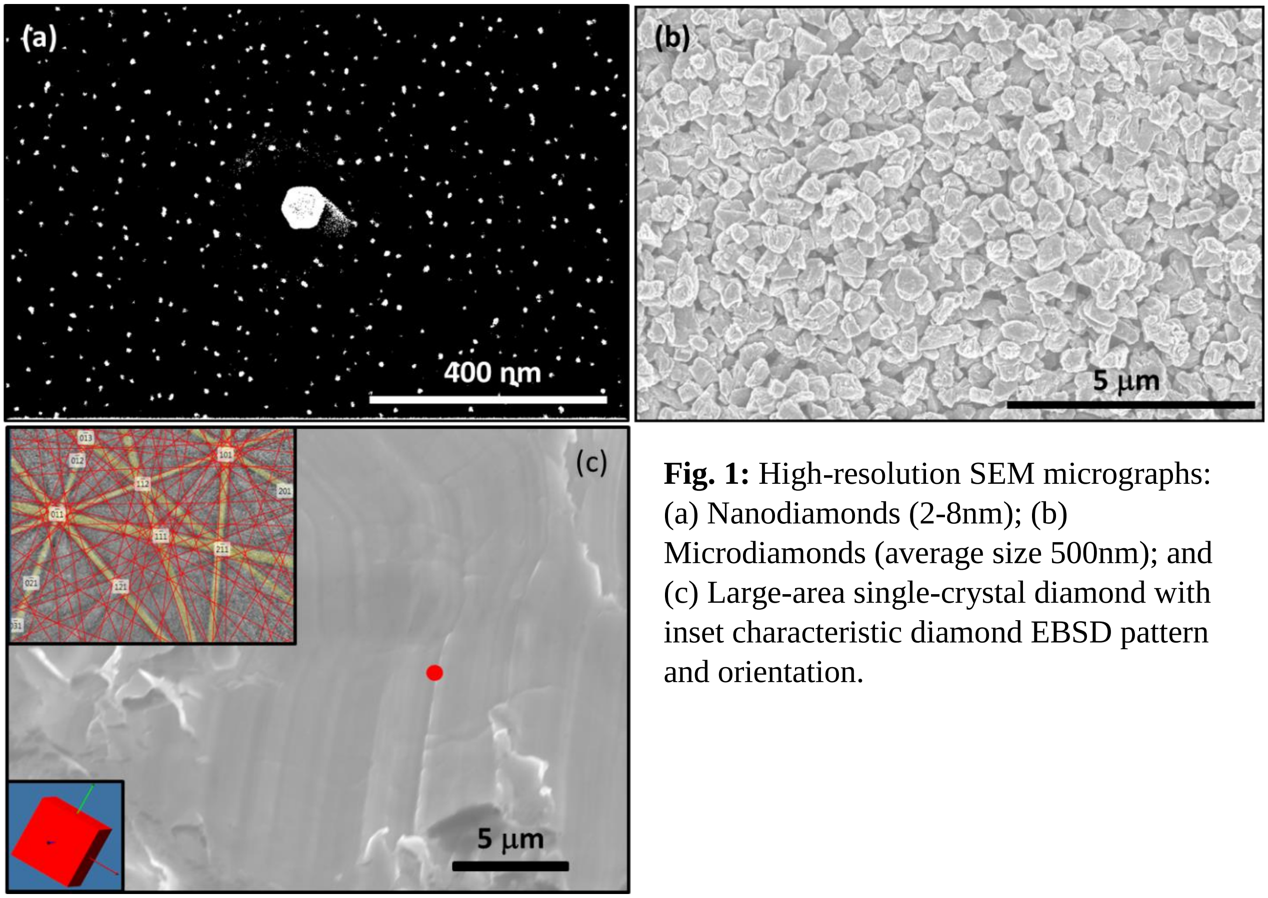

Fig. 1: High-resolution SEM micrographs: (a) Nanodiamonds (2-8nm); (b) Microdiamonds (average size 500nm); and (c) Large-area single-crystal diamond with inset characteristic diamond EBSD pattern and orientation.

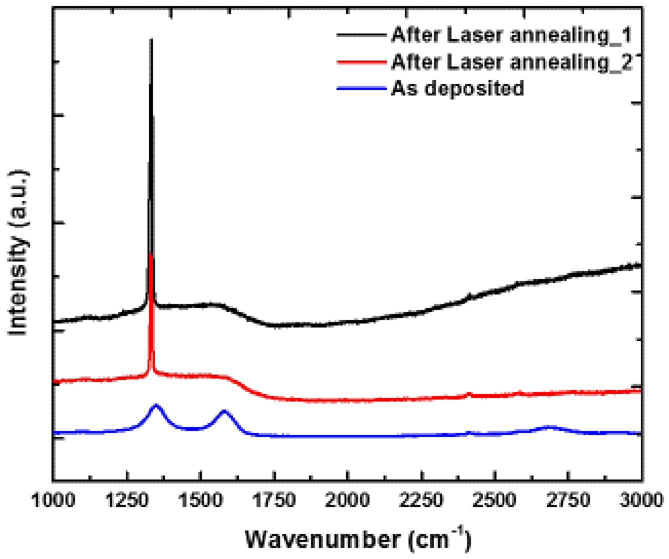

Fig.2: Raman spectra (633nm source) from as-deposited carbon films and after laser annealing with diamond peaks.

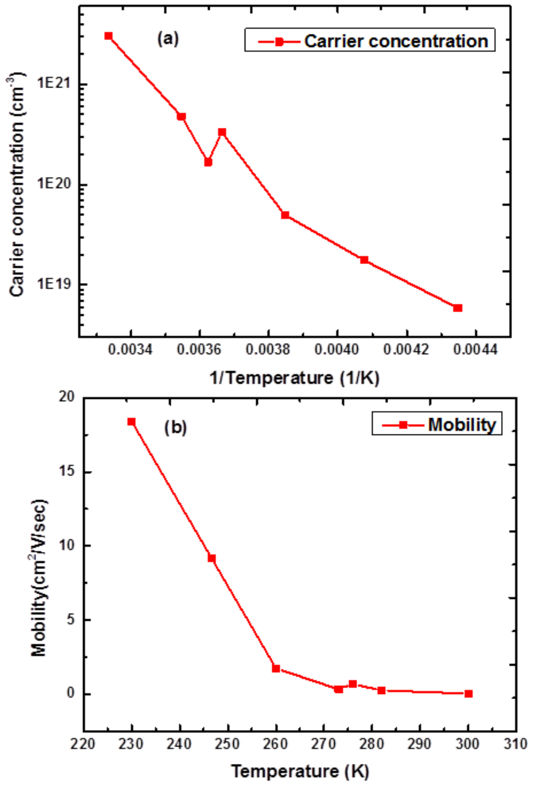

Fig. 3: (a) Carrier concentration plotted as 1/T; and (b) Hall mobility as a function of T.

Fig 3(a) shows preliminary results on carrier concentration in N-doped diamond plotted as a function of (1/T). The carrier concentration was found to vary from $2.0\text{x}10^{18}$ to $5.0\text{x}10^{21}\text{cm}^{-3}$. These high concentrations result of dopant trapping during rapid quenching from liquid phase into diamond. In the case of silicon, dopant concentrations exceeding four hundred times the solubility limits have been achieved as a result rapid solidification from the liquid phase. This phenomenon of formation of supersaturated silicon semiconductor alloys was modeled by solute trapping concepts. The carrier mobility as a function of temperature for a sample with carrier concentration $2.0\text{x}10^{19}\text{cm}^{-3}$ is shown in Fig. 3(b). This corresponds to conductivity of $\sim 25\Omega\text{cm}^{-1}$ at 250K, which quite reasonable. A fit to $n = \exp(-\Delta E/kT)$ suggest $\Delta E \sim 530\text{eV}$. While these results are encouraging, systematic in-depth studies are needed to unravel these complex doping phenomena.

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