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Enhanced nucleation and post-growth investigations on HFCVD diamond films grown on silicon single crystals pretreated with Zr:diamond mixed slurry

A.K. Dua, M. Roy*, J. Nuwad, V.C. George, S.N. Sawant

Novel Materials & Structural Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

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Abstract

Two sets, one deposited for ~20 min and other for ~1 h of diamond thin film samples are prepared following pretreatment of silicon substrates using mixed slurry containing different weight ratio of zirconium and diamond particles. The films are characterized ex situ using XRD, Raman spectroscopy, photoluminescence (PL), FTIR and atomic force microscopy (AFM). As evidenced from AFM topography, nucleation density as high as 2.5×10^9 particles/cm^2 could be achieved in spite of posttreatment cleaning of the substrates with methanol. It has been found that the nucleation density increases, while particle size and RMS surface roughness subsides with increasing metal concentration in the mixed slurry. Raman and PL spectra of both the 20 min and 1 h samples have been recorded to check the quality of the deposits. Although a significant amount non-diamond carbon impurities is found to be present mostly at the grain boundaries of the films, the concentration of defects due to [Si-V]^0 complex reduces substantially for full-grown samples and also for 20 min samples pretreated with metal-rich slurries. The plausible role of the intermediate layers behind these effects has been explored.

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Keywords: Substrate pretreatment; Zr:diamond mixed slurry; Nucleation; HFCVD; Diamond films

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1. Introduction

Some very recent and exciting applications of polycrystalline diamond thin films such as X-ray lithographic masks, micro/nano electro-mechanical systems (MEMS/NEMS), etc. require the films to be smooth, relatively defect and impurity free, continuous even at sub-micron thickness and at the same time be able to deposit on appropriate non-diamond substrates such as silicon etc. But owing to its very high surface energy, nucleation density of diamond on pristine silicon is rather low [1] ~10^4 particles/cm^2 under standard conditions of CVD deposition. This badly affects the properties, morphology and homogeneity of the deposited films because it is only during the nucleation stage that the density of diamond particles, alignment of the crystallites and many such important properties are determined. Therefore in order to improve such low nucleation a variety of surface pretreatments [2–9] are

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* Corresponding author. Tel.: +91-22-25590292; fax: +91-22-25505151.
E-mail addresses: mainak73@apsara.barc.ernet.in, mainak73@yahoo.com (M. Roy).

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given to the substrates such as damaging the surface either by mechanical or ultrasonic abrasion with diamond or other hard powders, seeding with diamond grits, ion implantation, applying negative bias, etc. Of the different methods employed for nucleation enhancement, ultrasonic pretreatment using diamond slurry is most commonly used because of the ease of its application to substrates having all sorts of complex geometry and shape and also the homogeneity in morphology of the films obtained upon deposition. Using mono dispersed diamond slurry alone though substantially increases [10] nucleation density ($\sim10^7$ particles/cm^2), the films deposited in general are quite rough and a continuous layer is obtained only after few hours of deposition. In contrast using polydispersed slurry composed of a mixture of small diamond and large metal particles [11], it is not only possible to attain very high nucleation densities ($\sim10^{10}$ particles/cm^2) but also obtain nanometer rough, sub-micrometer thick continuous diamond films in very short deposition times (even less than 20 min). Although the mechanism of this enhancement is still unclear and highly debated [12], it is primarily suggested that formation of highly reactive surface damage sites [13] due to the impact of large metal particles with simultaneous seeding of diamond [14], formation of a stable carbide interlayer and catalytic hydrogenation of non-sp^3-bonded carbon species to sp^3-bonded stable diamond precursors by transition metals [11] together contribute towards enhancement of nucleation. However, the possibility of heterogeneous nucleation of diamond on non-diamond materials such as cubic-BN, MoB, LaB_6 and TaB_2, SiC, etc. may not be ignored since pretreatment of substrates with these abrasives alone also offer substantial nucleation enhancement and in some cases even leading to textured growth of diamond films [15]. Therefore the choice of metals and/abrasives for mixed diamond slurries is required to be made judiciously. So far a large number of metals and metal carbides such as W, Ta, Mo, Nb, Ti, Al, Fe, Ni, Cu, Si, TaC, SiC, etc. in conjugation with diamond particles have been investigated for nucleation enhancement of which Ti reportedly yields the best results. Zr comes next to Ti in the same group of the periodic table and its catalytic activity as evidenced from the heats of chemisorption of different gases [16] is at par with that of Ti. Besides Zr is ~1.4 times denser than Ti and forms stable cubic carbide phase with lattice constant close to that of diamond. Thus it might be of considerable interest to explore its potential in enhancing diamond nucleation. Moreover, it is equally important to understand the effect of mixed slurry treatment on the growth of diamond films and hence characterize the full-grown films deposited following such substrate pretreatment. Surprisingly however there are hardly any references in the literature on the detailed post-deposition characterization of such films. In this article, we report on the nucleation enhancement of diamond induced by zirconium:diamond mixed slurry treatment of silicon single crystal substrates and post-growth characterization of diamond films thus deposited.

2. Experimental

Substrates used are one side polished, p-type, Si single crystal wafers from Wacker Chemitronic, GmbH, having (1 1 1) crystallographic orientation. First they are thoroughly degreased by sonicating in trichloroethylene followed by acetone and isopropyl alcohol, each time for ~5 min. Then they are subjected to a 2 min etch in 40% HF to remove the native oxide layer. Subsequently the substrates are sonicated in zirconium:diamond mixed slurries for ~30 min and then for another 5 min in methanol to remove any loose particles. These are dried and finally loaded for deposition. Slurries are prepared in 10 ml methanol by mixing fine diamond particles (size < 0.2 μm) with coarse zirconium metal particles (size ~ 50 μm) in different weight ratios. The HFCVD facility used for deposition is described elsewhere [17] and the optimized deposition parameters are detailed in Table 1. Two series of diamond thin films, one deposited for ~20 min and the other for ~1 h are prepared on silicon substrates pretreated with mixed slurries containing different zirconium:diamond weight ratio (viz. 0.5,1, 2 and 4). All characterizations of the samples are done ex situ. XRD patterns of the samples are recorded in a Philips X-ray diffractometer PW 1710 using Cu Kα line from an X-ray generator operated at 30 kV and 20 mA. Both photoluminescence and Raman spectra of the samples are recorded in a Labram-I (ISA make) spectrometer in a back scattering geometry with a spectral resolution of 2 cm^{-1}. The 488.0 nm

Table 1
Deposition parameters used for sample preparation

Parameters	Optimized values	Measuring probe
Base pressure	10^{-5} Torr	Discharge gauge
Working pressure	40 Torr	Strain gauge
H_2 (99.999%) flow rate	400 sccm	Mass flow controller
CH_4 (99.9%) flow rate	3 sccm	Mass flow controller
Filament (W helix, 5 mm diameter, nine turns, 0.5 mm wire diameter)		
Filament temperature	2050 °C	2C optical pyrometer
Substrate–silicon single crystal wafer		
Substrate temperature	850 °C	Pt, Pt–14% Rh thermocouple
Filament–substrate distance	~7 mm	
Deposition time	~20 min, ~1 h	

(~2.54 eV) line of an Ar^+ laser is used for excitation and the Raman scattered light is analyzed using a charge coupled device (CCD) camera for multichannel detection. AFM studies are carried out under ambient conditions using a scanning probe microscope (SPM-Solver P47, NT-MDT, Russia) in contact mode using rectangular silicon nitride tips (tip radius ~ 10 nm).

3. Results and discussion

Fig. 1(a)–(c) depicts the AFM topography of the samples grown for ~20 min, where from nucleation density; average particle size (geometric mean of the major and minor axes) and root mean square (RMS) surface roughness of the pretreated samples are estimated over a (5 μm × 5 μm) area using a dedicated software built in with the AFM instrument. The nucleation density in all the samples is found to be very high ~10^9/cm^2 (absolute value again depends very much on the experimental conditions), which is about two orders of magnitude higher as compared to samples pretreated with diamond slurry (~30 μm) alone and more than five orders of magnitude higher as compared to untreated pristine silicon substrate. It is to be noted that this high nucleation density could be achieved in spite of the fact that the substrates were thoroughly cleaned by sonicating in methanol after the mixed slurry treatment, as posttreatment cleaning is known to reduce the concentration of residual diamond particles and hence has a negative effect on diamond nucleation. The nucleation density has been found to increase monotonically with the increasing metal contribution in the mixed slurry (Fig. 2(a)) and no ‘‘Yarbrough’’ type of negative effect on nucleation

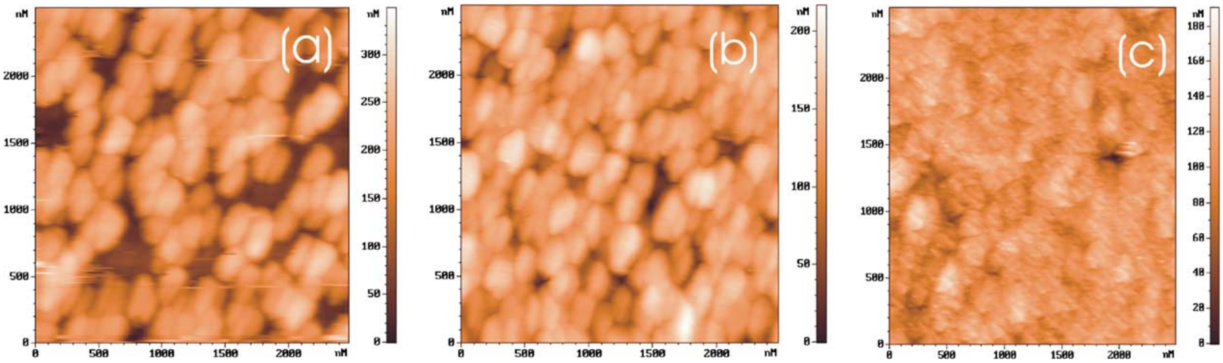

Fig. 1. AFM topography of samples deposited for ~20 min after pretreatment of the substrates with mixed diamond slurries containing different zirconium:diamond weight ratio: (a) 0.5, (b) 2 and (c) 4.

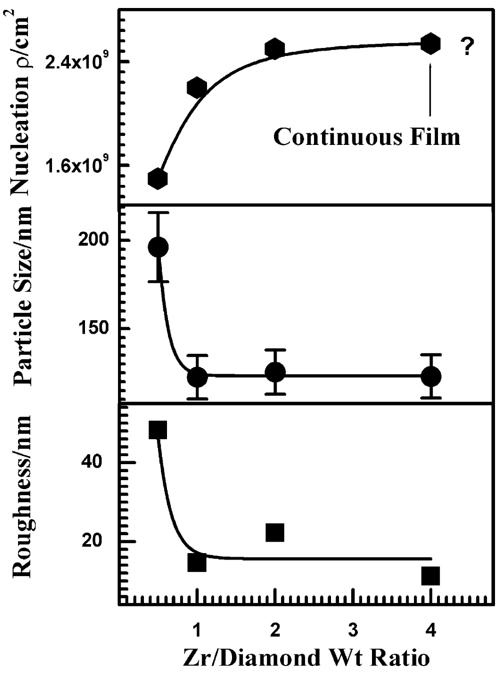

Fig. 2. Plot of: (a) nucleation density, (b) average particle size and (c) RMS surface roughness of the 20 min samples vs. zirconium:-diamond weight ratio in the mixed slurries.

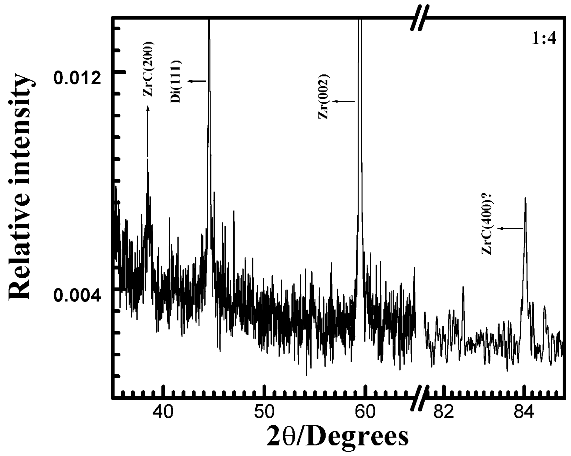

Fig. 3. A typical XRD pattern for the 20 min samples pretreated with metal-rich slurries.

[18], due to the metal particles etching out the existing nucleation sites is observed for the range of metal:-diamond concentration studied. For the sample treated with (Zr:Di = 4) slurry, a continuous film is obtained even in less than 20 min. Moreover, the crystallites tend to grow smaller in size (Fig. 2(b)) and the films become smoother (Fig. 2(c)) when the substrates are pretreated with higher concentration of metal in the mixed slurry. This is in contrast to what is expected if larger metal particle residues would have contributed towards particle size or surface roughness of the films. This implies that within 20 min of deposition, most of the metal and diamond particle residues get covered possibly due to the formation of continuous and smooth over layers. However, there is a sharp rise in particle size and surface roughness for the sample treated with (Zr:Di = 0.5) slurry and can be accounted for the formation of an entirely different kind of interlayer. A direct support to our speculation comes from the XRD patterns of the samples. Except for the one treated with (Zr:Di = 0.5) slurry, XRD patterns of all the 20 min samples exhibit (Fig. 3) distinct peaks at $\sim 2\theta = 38.42^\circ$, 44.5° and 59.5°, respectively, characteristic of the (2 0 0) planes of zirconium carbide (ZrC) (1 1 1) planes of diamond and (0 0 2) planes of zirconium metal indicating of the formation of a ZrC interlayer along with un reacted metal and diamond particle residues. The diamond XRD peak is however shifted slightly to higher 2θ values because of the compressive stress developed in the films due to lattice mismatch with ZrC interlayer. Transmittance FTIR spectra of the samples (not shown here) on the other hand exhibit intense features corresponding to the TO and LO modes of SiC for the sample treated with (Zr:Di = 0.5), which drastically reduces in intensity for samples treated with higher Zr:Di ratio. Thus it is clear that a SiC interlayer is predominantly formed in case of samples pretreated with diamond-rich slurries, while ZrC interlayer forms when treated with metal-rich slurries. Moreover, the broad peak at $\sim 1100\ \mathrm{cm}^{-1}$ that appears as a weak feature in the IR spectra of the former sample gets significantly enhanced in case of the later. This peak originating from the interstitial oxygen precipitated in most Czochralski (CZ) grown silicon wafers reportedly increases in intensity with the increasing concentration of point defects within the substrates. This indicates that in case of samples treated with metal-rich slurries, hammering effect by large metal particles produces greater concentration of defects within the substrates thereby facilitating diamond nucleation on them.

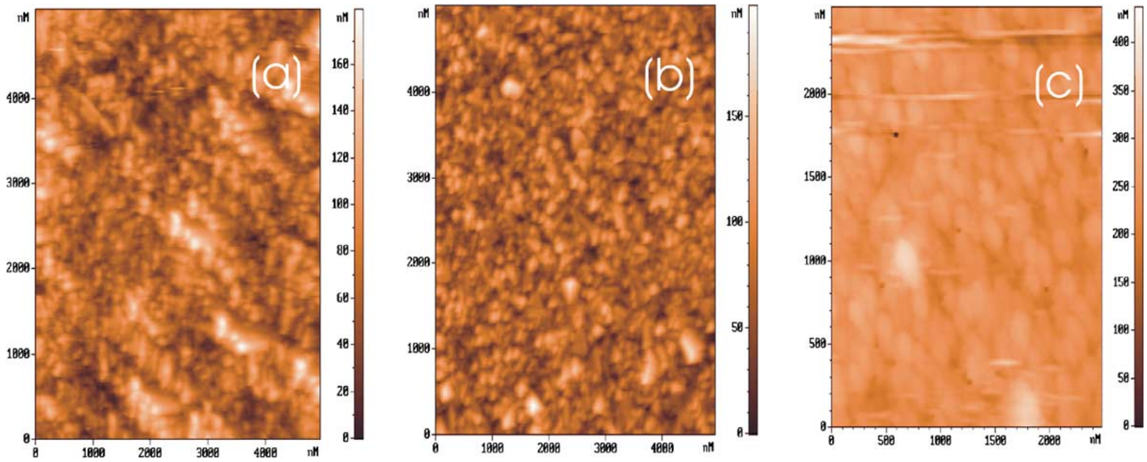

Fig. 4. AFM topography of samples deposited for ~1 h after pretreatment of the substrates with mixed diamond slurries containing different zirconium:diamond weight ratio: (a) 0.5, (b) 2 and (c) 4.

Within 1 h of deposition, multiple layers of continuous diamond films (characterized thoroughly by XRD and Raman) are formed on top of all the pretreated substrates. Fig. 4(a)–(c) shows the AFM topography of three such samples. Although the films are a micron thick now the average particle size has grown only 1.3 times bigger (~175 nm) and their RMS surface roughness varies in the range of (15–35 nm). The particle density on the top layer of the films has also been estimated and is typically of the order of 10^9 particles/cm^2, similar to that exhibited by the 20 min samples. This indicates that (as also can be clearly seen from the AFM images) there still exists a large number of grain boundaries in the films as the small diamond particles could not coalescence into bigger ones, possibly being prevented by the packed inter grain deposit of amorphous non-diamond carbon that in turn adds to the smoothness of the films. Moreover, in contrast to the samples deposited for ~20 min, here the variation of the average particle size and RMS surface roughness with (Zr:Di) ratio in the mixed slurry is quite subtle, which further indicates that the mixed slurry treatment affects strongly the nucleation stage only and its effect does not extend to the growth stage of deposition. Fig. 5(a) and (b), respectively, shows the XRD patterns of the 1 h samples deposited upon pretreatment with minimum and maximum concentration of Zr in the mixed slurry used in the present study. Clearly all the patterns exhibit an intense peak at $\sim 2\theta = 44.5^\circ$ unambiguously assigned to the (1 1 1) planes of diamond and also features corresponding to both zirconium carbide and metallic zirconium. Clearly the peaks corresponding to ZrC become much more intense for samples pretreated with increased metal-rich slurries, thereby indicating of their greater tendency to form metal carbides. However, no diffraction lines characteristic of SiC phase could be detected for any of these samples. Apart from nucleation density and surface roughness of the films, the film-properties that are of utmost importance and need to be closely monitored are the quality of deposited diamond, the crystal defects developed during growth process and the fraction of non-diamond carbon impurities co-deposited along with diamond. Raman spectroscopy is by far the most

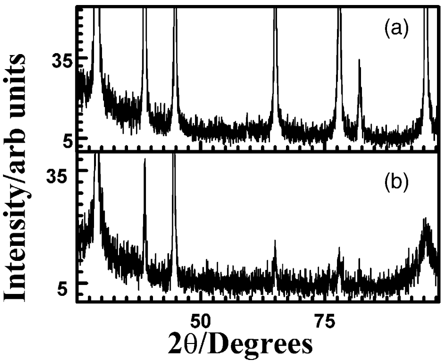

Fig. 5. XRD patterns of ~1 h samples after pretreatment of the substrates with (a) Zr:Di = 4 and (b) Zr:Di = 0.5 slurries.

versatile non-destructive technique available for characterization of different forms of carbon. Cubic diamond has a single Raman-active first order phonon mode at the center of the Brillouin zone. The sharp line that appears at 1332.5 cm^{-1} with FWHM of less than 2 cm^{-1} for natural diamond gets significantly broadened and shifted to higher wave numbers in case of polycrystalline diamond films. This shift in the Raman line often correlates well with the compressive or tensile stress developed in the films especially when grown on non-diamond substrates and under extreme conditions of biaxial stresses even the degeneracy of this triply degenerate phonon is lifted up. The line width on the other hand is related to the degree of structural order in the film micro crystallites and has been found to depend very much on the film preparation conditions. The Raman spectra of our samples deposited for ~20 min and ~1 h are, respectively, shown in Fig. 6(a) and (b) both normalized to the intensity of their respective 521 cm^{-1} 1st order silicon peak. In all the spectra apart from the t_2g Raman band at 1332 cm^{-1}, two broad features centered at ~1350 and 1550 cm^{-1} and a high-energy shoulder between 1590 and 1610 cm^{-1} are also observed. The peaks at ~1350 and 1550 cm^{-1} corresponds to the D and G bands of diamond-like carbon (DLC), while the hump between 1590 and 1610 cm^{-1} has been ascribed to the first order zone boundary phonon. It appears due to the break down of the $k = 0$ selection rule in small sized DLC particles and has been reported to have the effect of shifting the wave number of the G band significantly. These small

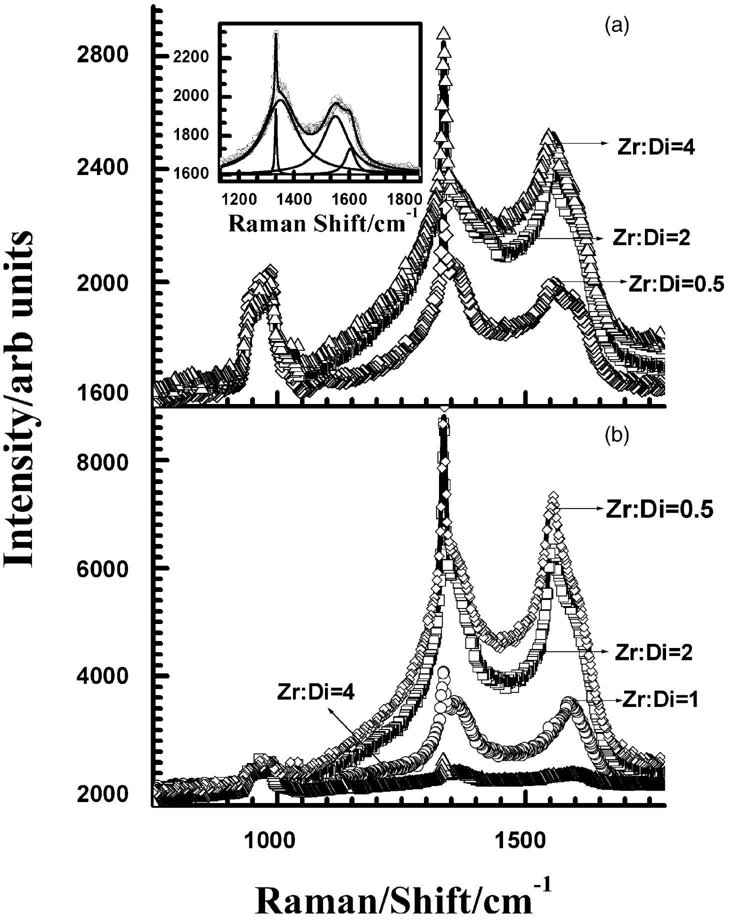

Fig. 6. Raman spectra of samples deposited for: (a) ~20 min and (b) ~1 h. Inset: a typical spectra fitted with Lorentzian line shapes along with its deconvoluted features.

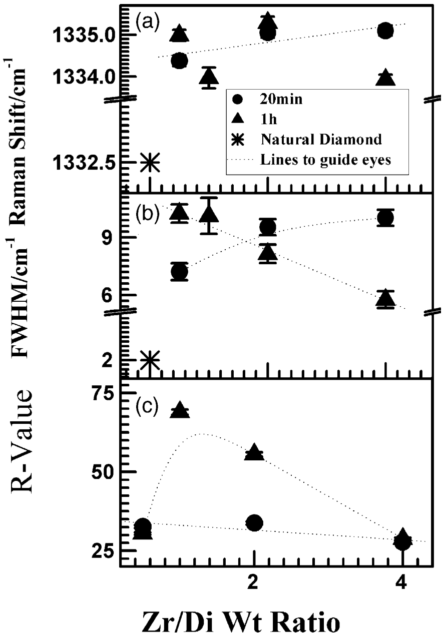

Fig. 7. Variation of: (a) Raman shift, (b) FWHM of diamond line and (c) the relative non-diamond content of the films (*R*-values) with zirconium:diamond weight ratio in the mixed slurry for both the sets of samples deposited for ~20 min and 1 h.

amorphous carbon particles tend to accumulate primarily at the inter grain boundaries. Thus substantial amount of non-diamond fragments even in samples grown for ~1 h clearly indicates the presence of a large number of grain boundaries in those films as has already been observed from the AFM images. Moreover, the 1332 cm^{-1} diamond peak changes in peak positions, FWHM and intensity for samples pretreated with slurries containing different Zr:Di weight ratio. In order to monitor such variation quantitatively the spectrum in the wave number range 1140–1850 cm^{-1} is fitted with four Lorentzian line shapes where from the peak position, FWHM and area under the respective curves are obtained in the form of fitted parameters. The inset in Fig. 6(a) shows a fitted Raman spectrum along with its deconvoluted features, a small χ^2 value indicating the goodness of the fit. The fractional non-diamond content of the films is determined from the ratio (*R*-values) of the integrated area of the spectrum in the specified range to the area under the 1332 cm^{-1} peak. Fig. 7(a)–(c) depicts the variation of the 1332 cm^{-1} Raman peak position, its FWHM and *R*-value as a function of zirconium:diamond weight ratio in the mixed slurry for both the sets of samples deposited for 20 min and 1 h. Clearly compared to that for natural diamond the diamond phonon lines here (Fig. 7(a)) appear at higher wave numbers and are substantially broadened (Fig. 7(b)) implying that a compressive stress is developed in the films. For the 20 min samples the blue shift of the diamond lines as well as their FWHM gradually increase with increasing Zr:Di weight ratio in the mixed slurry. This may again be explained on the basis of different interlayers formed upon pretreatment with different mixed slurries. SiC ($a = 4.359$ Å) mainly formed with diamond-rich slurries has a lower lattice mismatch with diamond ($a = 3.567$ Å) as compared to ZrC ($a = 4.693$ Å), formed preferentially with metal-rich slurries and hence it offers lesser amount of stress to the diamond layer growing on top of it. On the contrary, the relative non-diamond content of the films for the 20 min samples as obtained from the *R*-values tend to decrease with the increasing Zr content in the mixed slurries. For the 1 h samples neither the diamond peak positions nor the *R*-values follow any statistical variations with Zr:Di weight ratio in the mixed slurry. The FWHM of the diamond peak however decreases steadily with increasing Zr concentration indicating of the improved crystallinity and decreased defect concentration in the films. Photoluminescence offers a very effective means of studying defects in CVD diamond films even in ppb levels. Present-day Raman spectrometers equipped with CCD detectors often allow simultaneous recording of Raman and PL spectra. However, the PL spectrum profile suffers from the system response, elastic light scattering illumination geometry, incident light intensity etc. Hence it is required to normalize the PL spectra to the integrated diamond peak for their semi-quantitative comparison between different samples. Fig. 8 shows the normalized PL spectra of our (a) 20 min samples and (b) 1 h samples. Apart from the Raman lines of diamond and amorphous carbon at ~2.37 and 2.35 eV, both the sets of spectra exhibit intense LO and TO Raman lines of silicon carbide at ~2.422 and 2.44 eV along with PL peaks at ~1.68, 1.964, 1.99, 2.02, 2.156, 2.182 and 2.2 eV. The intense peak at ~1.68 eV is the well-known signature for silicon–vacancy complex and the small feature at ~2.156 eV has been assigned to the $[N\text{-}V]^0$ center. The remaining host of peaks possibly originates from the transition between different

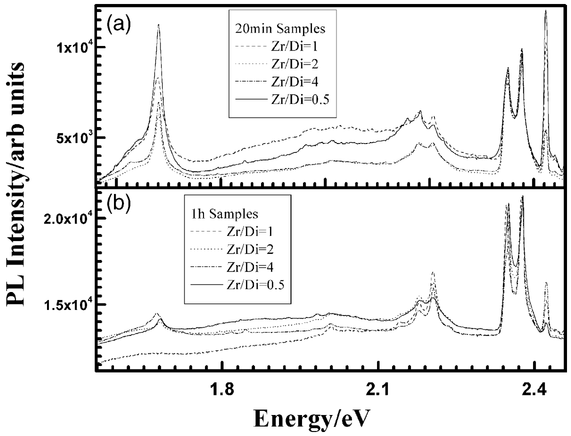

Fig. 8. Photoluminescence spectra of diamond thin film samples deposited for: (a) ~20 min and (b) ~1 h.

excited and ground states of an impurity stabilized triplet ($S = 1$) divacancy center. For 20 min samples (Fig. 8(a)) the intensity of both the TO and LO Raman peaks of SiC gradually decrease on being pretreated with more and more metal-rich slurries. This further confirms our previous conclusion from FTIR studies on the formation of different kind of interlayers upon pretreatment with different mixed slurries. The 1.68 eV PL peak intensity due to silicon–vacancy complex also decreases with Zr concentration in the mixed slurry and may be explained on the basis of slower diffusion rates of silicon across ZrC interlayer predominantly formed when treated with metal-rich mixed slurries. But no systematic trend of variation could be observed for the PL spectra of 1 h samples thereby confirming again that nucleation and growth stages are differently affected by mixed slurry pretreatment. However, there is a net decrease in the PL peak intensity of the defect centers in case of 1 h samples suggesting a steady decrease in their concentration as the film grows.

4. Conclusions

As anticipated, Zr behaves very much like Ti in the mixed diamond slurry pretreatment of silicon substrates for enhancement of diamond nucleation on them. Presently nucleation density as high as 2.5×10^9 particles/cm^2 could be achieved in spite of post-treatment cleaning of the substrates with methanol. For samples deposited for ~20 min, the nucleation density increases and the particle size and RMS surface roughness decrease with Zr:Di weight ratio in the mixed slurry. It has been shown from XRD studies that a stable ZrC interlayer is formed on the pretreated substrates, which supposedly plays a crucial role in controlling these parameters. It could also be seen both from XRD and Raman studies that a significant amount of compressive stress is developed in the films deposited for ~20 min, that increases for samples pretreated with metal-rich slurries. Moreover, a very large number of grain boundaries is found to exist in all the films deposited for both 20 min and 1 h that acts as sites for non-diamond amorphous carbon impurities. Again in 20 min samples the concentration of defects due to the formation of silicon–vacancy complex decrease on being pretreated with metal-rich slurries and it has been attributed to the slower diffusion of silicon across the ZrC interlayer. However, all these effects of metal pretreatment on the different properties of full-grown diamond films (deposited for ~1 h) is found to be quite subtle, which confirms that it strongly affects the nucleation stage only and not the growth stage of film deposition.

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