

Effect of pre-annealing on the structural evolution and optical response of Ag films exposed to iodine vapours

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Abstract. Ag thin films of 5 nm thickness were deposited on glass substrates by thermal evaporation. The films were divided into two sets, out of which, one set was not annealed and the other set was subjected to pre-annealing at 300°C for 2 h in air. The un-annealed and pre-annealed films were exposed to iodine vapours at room temperature for the durations from 5 min to 10 h. The un-annealed films were crystallized into the β phase of AgI after exposure for 5 h. In contrast, for the pre-annealed films, crystallization into the β phase occurred within the first 5 min. Both sets of films, however, exhibit a strong preferential *c*-axis orientation in the β -AgI phase. Optical absorption studies reveal that the un-annealed films exhibit a localized surface plasmon resonance (LSPR) with a peak at 545 nm and a long wavelength shoulder at 620 nm, which shifts to 516 nm after iodization for a few minutes. This peak position does not change with further iodization. The LSPR for the pre-annealed films has a single peak at 538 nm. After iodization for a few minutes, this peak shifts to 525 nm. Iodization for 3 h results in a further blue-shift of this resonance to 475 nm. The photoluminescence spectrum reveals two peaks, one at 368 nm and the other at 712 nm. The first one is assigned to the excitons of AgI, whereas the long wavelength peak is attributed to the presence of disorder in the films. The reasons for the difference in behaviour of the un-annealed and pre-annealed films are discussed.

Keywords. AgI; thin films; iodization; annealing effects.

1. Introduction

Silver iodide (AgI) exists in four different polymorphic forms, which are: (1) a low-temperature cubic form with the sphalerite structure, (2) a hexagonal wurtzite structure, (3) a high-temperature body centred cubic structure and (4) a high-pressure sodium chloride-type cubic structure [1]. This makes AgI amenable for application in a variety of technologies. The use of AgI in photography due to its extreme photosensitivity, in cloud seeding, the superionic and photocatalytic properties are well documented [2–5]. AgI in the form of thin films have shown potential for application in resistive memories and optical waveguides [6–10]. One of the facile approaches to the formation of AgI thin films is the iodization of Ag films at room temperature for durations ranging from a few seconds to several hours [11–18]. Iodization was shown to cause significant structural and microstructural changes that lead to extremely interesting optical properties. The extent of iodization can be used to control the local surface plasmon resonance (LSPR) of Ag. There is evidence for photoluminescence (PL) that is also dependent on the extent of iodization of Ag. The formation of AgI by iodization leads to a very interesting situation wherein, depending on the extent of iodization, a composite of Ag/AgI

is formed, which enables the study of properties of both Ag and AgI.

The literature on the evolution of iodized Ag films focusses mainly on as-deposited and doped films [11–18]. However, not enough attention was paid to the annealing of the Ag films prior to iodization. Hence, in this study, we report a study of iodization of two types of Ag films. Ag films of 5 nm thickness are deposited on glass substrates by thermal evaporation. These films are post-deposition annealed at 300°C, followed by iodization of both sets of films for duration up to 12 h. The extent of iodization is followed by X-ray diffraction (XRD). The nature of surface plasmons in Ag films was investigated using absorption spectroscopy and excitons in AgI were studied by PL spectroscopy. The evolution of Raman spectra and dependence on extent of iodization were also discussed. To the best of our knowledge, there are no other reports on the properties of pre-annealed Ag films exposed to iodine vapours.

2. Experimental

Thin films of Ag were deposited on glass substrates by resistive thermal evaporation carried out in vacuum better than

4×10^{-5} mbar and rate of deposition between 0.1 and 0.5 \AA s^{-1} without intentionally heating the substrates. The glass substrates were first cleaned with acetone and ethanol and then, rinsed with ethanol in an ultrasonic cleaner for 20 min prior to each deposition. Ag wire (99.9% pure) was placed in a tungsten spiral boat. The substrates were placed in the holder at a distance of 10 cm from the source. The as-deposited films are termed as Ag-U in the rest of the article. The substrates were retained in the same vacuum for 1 h after completing the deposition process. Some of these films were subjected to post-deposition heat treatment at 300°C for 2 h in air. These films are termed as Ag-A, in the rest of the article. Thickness of the films, estimated using a quartz crystal thickness monitor, was 5 nm. All these films (Ag-U and Ag-A) were then subjected to iodization at room temperature for period up to 12 h.

The spectral transmission curves were recorded in the wavelength range of 200–1200 nm in a UV–VIS–NIR spectrophotometer (Elico model no. SL 159). The crystal structure of the films was obtained from a powder X-ray diffractometer (XRD) (Philips PW 1830 with $\text{CuK}\alpha$ radiation of wavelength 0.15406 nm). Raman spectra were recorded in a confocal micro-Raman spectrometer (Alpha 300 of Witec, Germany) equipped with a second harmonic Nd-YAG laser excitation source of 532 nm wavelength. Atomic force microscope (AFM) images were acquired in a NT-MDT Model Solver Pro microscope in the contact mode. The excitation and luminescence spectra were investigated by Edinburgh UV–VIS–NIR (FLS 980) spectrometer with xenon arc lamp (250 W) as an excitation source.

3. Results and discussion

XRD patterns of the Ag-U thin films iodized for time intervals from 0 to 10 h are shown in figure 1a. The un-iodized pure Ag films did not exhibit any crystallinity. The onset of crystallization was observed after iodization for 5 h with the appearance of three diffraction peaks that can be assigned to (002), (100) and (101) planes of hexagonal $\beta\text{-AgI}$ (JCPDS card number 85-0801). A survey of literature shows that there is an overlap in the peak positions of (002) plane of $\beta\text{-AgI}$ and the (111) plane of $\gamma\text{-AgI}$. However, the appearance of ‘triplet’ of the peaks corresponding to the (100), (002) and (101) planes unambiguously confirms the formation of $\beta\text{-AgI}$. Interestingly, when the duration of iodization was increased to 10 h, a structural phase transformation to the cubic $\gamma\text{-AgI}$ structure was observed.

XRD patterns of the Ag-A films, as a function of duration of iodization, are shown in figure 1b. There is a remarkable difference in the crystalline evolution of the Ag-U and Ag-A films. In the Ag-A case, onset of crystallization is observed after a very short iodization duration of 5 min as evidenced by the appearance of the diffraction peak that can be assigned to the (002) plane of hexagonal $\beta\text{-AgI}$. Furthermore, after 3 h of iodization itself, there is evidence for strong preferential

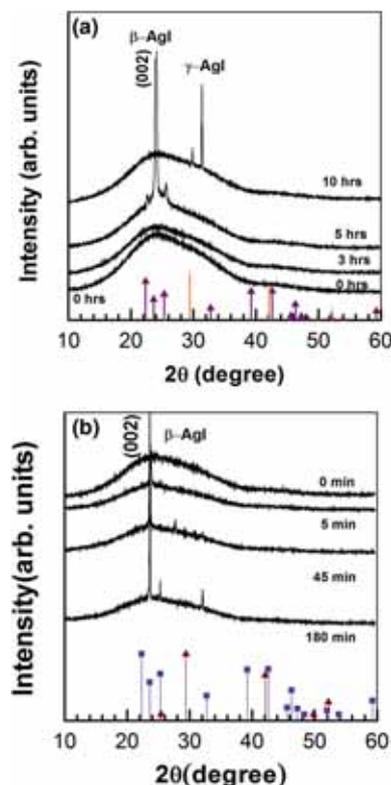


Figure 1. X-ray diffraction patterns of the (a) Ag-U and (b) Ag-A films iodized for different durations. Also shown are the standard patterns for $\beta\text{-AgI}$ (JCPDS card no. 85-0801) and $\gamma\text{-AgI}$ (JCPDS card no. 78-0749).

orientation as compared to the 5 h of iodization required for the Ag-U films. It is important to note that the un-iodized Ag-A film does not show any evidence for crystallinity as in the case of Ag-U films. Another observation is that the diffraction peaks of AgI are superimposed over a largely amorphous background for all durations of iodization. There are two sources for the amorphous background: (1) the amorphous glass substrate and (2) incomplete crystallization and disorder in the AgI. The origin of the difference in crystallographic evolution of the Ag-U and Ag-A films could also be microstructural in nature, since all other conditions are same. Therefore, the microstructure of the un-iodized Ag-U and Ag-A films was examined.

Earlier work on iodization of thermally evaporated and sputtered Ag films by Sunandana and co-workers [11–17] has shown that this form of iodization leads inevitably to the formation of $\gamma\text{-AgI}$. The difference in observations between the current and earlier works is due to difference in processing parameters leading to morphological variations and, therefore, the resultant crystallographic texture. One of the main differences is in the rate of deposition, which is much lower in the present case. Secondly, the films reported by these authors were generally discontinuous, which is not true for the present work. It is also observed by these authors that the absence

of intrinsic stacking faults is a necessary condition for the formation of γ -AgI. Evidently, in the present case, the thermodynamic conditions required for the formation of γ -AgI are available only after extended durations of iodization (>6 h in the Ag-U case and >3 h in the Ag-A case). These results, however, are similar to those reported by Bashouti *et al* [18], who have reported the formation of *c*-axis-oriented β -AgI in iodized sputtered Ag thin films of similar thicknesses.

The absorption spectra of Ag-U films iodized for 0–10 h are shown in figure 2a. The un-iodized Ag films exhibit a broad peak in the absorption spectrum centred around 545 nm, which is attributed to a LSPR. The half width of the peak is >150 nm, indicating the large dispersion in particle size of the Ag films. There is a shoulder at 620 nm indicating the presence of higher order resonances and non-spherical shapes of particles in the films. The position and width of LSPR peaks are known to be extremely sensitive to the shape, size and separation between particles. After iodization for about 60 min, there is suppression of the LSPR peak and emergence of a broad feature that is blue-shifted from the LSPR peak of un-iodized Ag to 520 nm. The suppression of LSPR and emergence of this feature is attributed to the excitons in β -AgI. This is in sharp contrast to the facile exciton formation in γ -AgI. Earlier reports have shown that this feature has a peak at 440 nm [11–18]. However, the large width of the peak suggests that the LSPR dominates over the excitonic peak leading to the co-existence of plasmons and excitons, caused by the incomplete iodization of the films.

The optical response of the Ag-A films to iodization, in contrast, is completely different as observed from figure 2b. The absorption spectrum of the un-iodized film is characterized by a single peak centred around 538 nm due to LSPR of Ag. Iodization of the films up to 45 min leads to a blue-shift in the LSPR peak to 525 nm, which does not change the spectrum. There is a further blue-shift in the LSPR peak position beyond 60 min of iodization to a value of 475 nm. It is accompanied by the appearance of a weak shoulder at 430 nm corresponding to the evolution of the excitons in β -AgI. The differences in the peak position of LSPR as a function of iodization times are plotted in figure 3. It is evident from this figure that the iodization process leads to two regimes of plasmonic behaviour in the case of Ag-U films and three regimes in the case of Ag-A films.

The first observation that can be made is that the annealing of un-iodized Ag films leads to blue-shifting of LSPR peak. Interestingly, in both cases, there is a blue-shift in the LSPR peak after initial iodization. In the case of Ag-U films, after the initial blue-shift, there is no further change in the peak position, intensity or width. However, in the case of Ag-A films, there is an initial blue-shift from 540 to 525 nm in the LSPR peak for the duration of iodization up to 45 min. This is followed by a further blue-shift in the LSPR peak to 475 nm. These blue-shifts are quite large reflecting the role of a fundamentally different mechanisms operating in quasiparticle formation. The blue-shifting is accompanied by a decrease in intensity of the LSPR peak for both sets of films. The

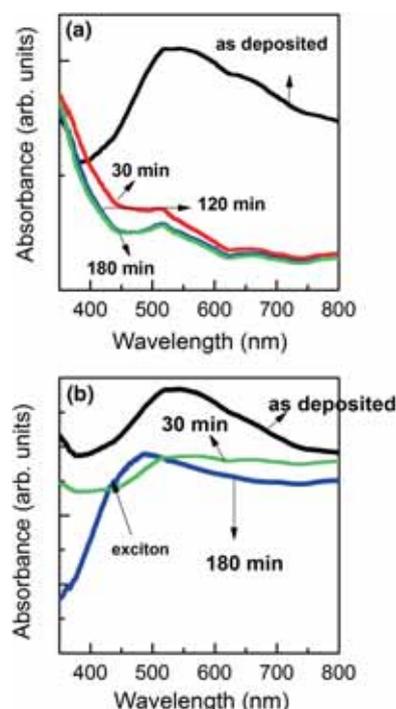


Figure 2. Optical absorption spectra for (a) Ag-U and (b) Ag-A films iodized for different durations (as-deposited corresponds to the un-iodized film).

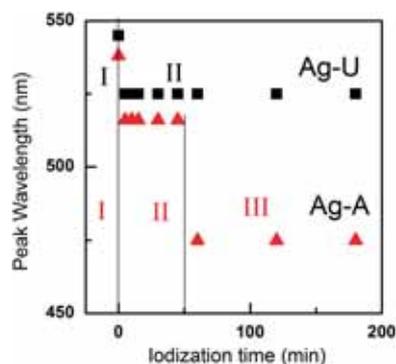


Figure 3. Variations in localized surface plasmon peak position as a function of iodization time.

blue-shift is a consequence of quantum confinement effects as a result of reduced particle size. Typical AFM images of the Ag-U and Ag-A films are shown in figure 4a and b, clearly indicating the differences in morphology.

The LSPR peak positions were compared favourably with those reported in the literature. Kumar and Sunandana [11–13] have reported LSPR peak at 420 nm, which evolves into an excitonic feature after brief iodization. The films in this case were also produced by thermal evaporation. Mohan and Sunandana [14,15] have reported similar SPR features in Ag films of 5–20 nm thickness that were iodized from 15 min to 60 h. Rajesh and Sunandana [17] have reported SPR peak

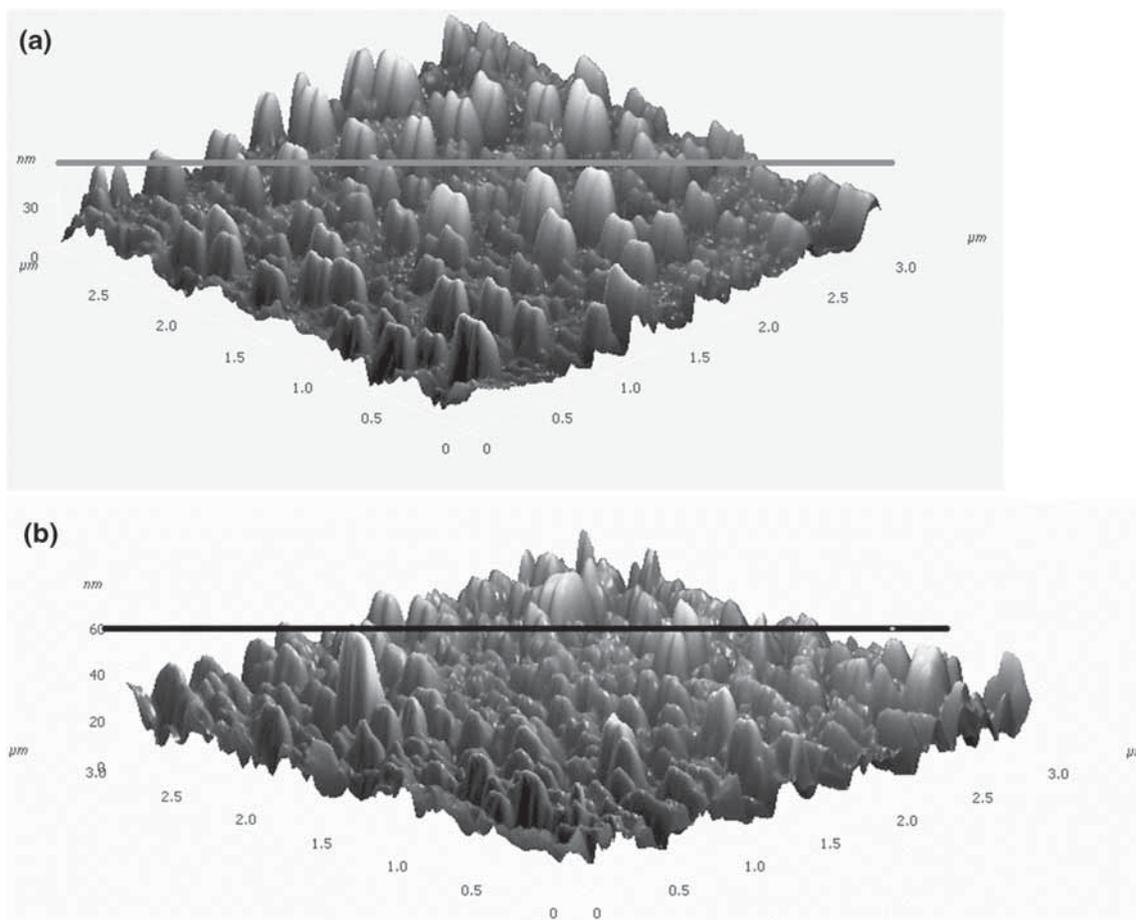


Figure 4. Atomic force microscope images of (a) Ag-U and (b) Ag-A films.

values ranging from 380 to 460 nm as a function of iodization time. The Ag films in this case were 30 nm thick and thermally evaporated onto glass substrates. Ag/AgI composites were formed by iodization. Bashouti *et al* [18] have reported a peak centred around 420 nm. Ghosh *et al* [19] have reported a SPR peak at 412 nm, which is suppressed by the formation of AgI, leading to the evolution of an excitonic peak centred around 420 nm. They observe shifting of the excitonic peaks depending on the environment around AgI. Clearly, the positions of the LSPR peak of Ag, as a consequence of iodization, are dependent on processing technique, duration of iodization and initial thickness of the films. The reason for attributing the observed absorption peaks to LSPR stems from the basic difference in the definition of SPR and LSPR. SPR refers to the process wherein the frequency of evanescent electromagnetic wave propagating at the metal–dielectric interface, is resonant with the oscillation of the surface conduction electrons in the metal. In contrast, LSPR is used when the system under consideration comprises metallic nanoparticles and there is resonance between frequencies of the incident photon and collective oscillations of conduction electrons in these nanoparticles. It is also important to note that SPR generally propagates, while LSPR is localized to a nanoscale region in

the vicinity of the particle. Since in the present case, the films consist of nanoparticles, the peaks are attributed to LSPR.

The effect of iodization on the PL spectra of the as-deposited Ag and Ag-A films was also studied. The PL spectra recorded using an excitation wavelength of 310 nm is shown in figure 5. The as-deposited pure Ag film displays a peak at 374 nm. In the case of the Ag-A films, there are two peaks with the first one centred around 368 nm (3.35 eV) and the long wavelength peak being centred around 712 nm (1.73 eV). The short wavelength peak was characterized by two other peaks at 449 (2.75 eV) and 466 nm (2.65 eV), respectively, as shown in the inset. The PL spectrum for the pure Ag film was very noisy beyond 600 nm and is therefore not presented.

Mochizuki and Fujishiro [20] have reported a strong luminescence peak due to the W_1 exciton, which followed low energy shoulders in pure crystals of β -AgI at 2.936 eV using 355 nm excitation. They also stated that the high intensity luminescence band is superposed on a skirt extending up to about 3.1 eV, and it is also accompanied by several shoulder components. The low energy shoulders are attributed to the radiative decay of excitons due to stacking faults. Shaker-Agjekandy and Habibi-Yangjeh [21] have observed two PL peaks at 450 and 470 nm using an excitation wavelength of

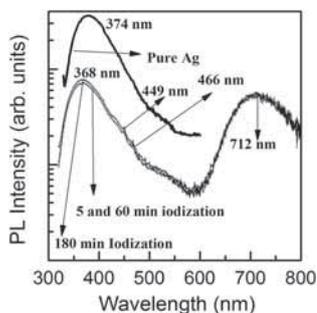


Figure 5. PL spectra of the Ag-A films iodized for 5, 60 and 180 min.

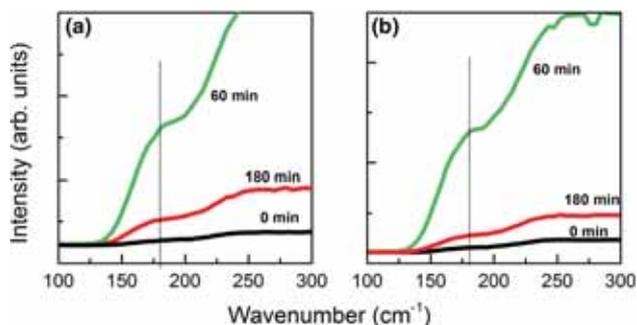


Figure 6. Raman spectra of (a) Ag-U and (b) Ag-A films iodized for durations as shown.

300 nm in AgI/ZnO nanocomposites. Choi *et al* [22] have reported a luminescence band that extends from 425 to 600 nm with a peak at 470 nm with excitation at 355 nm. Liang *et al* [23] have examined the PL spectra of AgI/Ag nanowire heterojunctions and have also reported a broad emission band in the 600–900 nm wavelength region. They have attributed this to the relatively high proportion of disordered AgI and the even more pronounced disordering of small-diameter AgI. The existence of disorder is evident from the XRD patterns presented in figure 1a and b, wherein the crystalline peaks due to β -AgI are superposed on a very broad amorphous background, independent of iodization time. The Raman spectrum of β -AgI exhibits the following modes: $A_1(\text{TO})$ and $E_1(\text{TO})$ at 106 cm^{-1} ; $A_1(\text{LO})$ and $E_1(\text{LO})$ at 124 cm^{-1} and E_2 mode at 17 and 112 cm^{-1} [24]. The Raman spectra recorded for the Ag-U and Ag-A samples in figure 6a and b show a weak shoulder around 185 cm^{-1} , but none of the other features were shown as mentioned earlier. This shift in the Raman peak and softening could be a consequence of the presence of unreacted Ag as well as the disorder in the films, discussed earlier. It is therefore, postulated that the broad emission long wavelength band observed in these films is also due to the presence of amorphous AgI. Another question that arises is the possibility of oxidation due to annealing of Ag. This cannot be ruled out, especially, in the case Ag-A films and is the subject of a concurrent study.

The model of growth that emerges from these observations is that the un-iodized films have large Ag agglomerates as is evident from the peak positions of the LSPR. Several studies have shown that the SPR of spherical Ag nanoparticles should appear at 450 nm [25–27]. However, in the present case, LSPR peaks for the Ag-U and Ag-A samples occur at wavelengths $>500 \text{ nm}$, indicating both non-spherical shapes and large particle sizes. Exposure to iodine vapours causes decrease in size of the Ag nanoparticles leading to a blue-shift in LSPR peak position. The concomitant decrease in intensity is due to the increase in inter-particle distance of Ag as a result of iodization. Thus, there are Ag nanoparticles embedded in an AgI matrix. As observed by other workers, exposure to iodine vapours leads to iodine-assisted crystallization of AgI into the β phase [18]. The considerable delay in the formation of excitons is perhaps a crucial clue to the unique growth of β -AgI crystals with high (001) orientation. There is an evidence for preferential c-axis orientation, which could be due to a free energy minimization process. Surprisingly, there appears to be disorder in the system, for which evidence is provided by the blue-shift in band edge related to PL peak and the appearance of a long wavelength feature attributed to disorder. These are features common to both Ag-U and Ag-A films.

The crucial difference between the un-annealed (Ag-U) and pre-annealed (Ag-A) films is in crystallization kinetics. While the onset of crystallization into the β -AgI is observed after 3 h in the Ag-U case, it happens within the first 20 min for the Ag-A films. The annealing process, thus, renders the Ag particles to be more reactive that present a lower energy barrier to crystallization. This is also evident from the fact that there are three regimes of LSPR behaviour for the Ag-A films as compared to the two regimes shown by the Ag-U films. Iodization, therefore, progresses for a longer duration leading to the continuous breakdown of Ag nanoparticles to smaller and smaller sizes. The saturation of the Ag surface due to iodization, i.e., the absence of chemically active sites, takes a much longer time for the Ag-A films. Pre-annealing of the Ag films is, thus, a more effective approach for the production of preferentially oriented AgI films. This study has dramatically demonstrated that a simple method of annealing can very effectively control iodization kinetics with respect to exciton formation and highly oriented β -AgI crystal growth observations that could trigger applicable technology development.

4. Summary

In summary, Ag thin films of 5 nm thickness were deposited on glass substrates by thermal evaporation followed by iodization at room temperature. The process of iodization and its impact on the structural evolution and optical response was investigated. Some of the Ag films were pre-annealed prior to iodization and it was observed that these were crystallized faster than the un-annealed films (5 min against 5 h). Iodization causes crystallization into β -AgI with a strongly preferred c-axis orientation. The plasmon resonance peak

of the un-annealed films exhibited a blue-shift from 545 to 516 nm, whereas the blue-shift was larger, from 538 to 475 nm, in the case of pre-annealed films. The PL spectrum reveals two peaks, one at 368 nm and the other at 712 nm. The reasons for the difference in behaviour of the un-annealed and pre-annealed films were discussed.

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