Arsenic ion implantation induced structural effects in C_{60} films

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C_{60} films grown on Si (001) by vacuum evaporation were implanted with 100 keV positive arsenic ions to various doses in the range 1×10^{13} to 1×10^{15} ions/cm^2. The structural properties of the implanted films were studied using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and atomic force microscopy (AFM). XPS results indicate the formation of arsenic buried layer within C_{60} film leading to the anisotropy stress in the film. XRD results reveal the preferential orientation of the film along the (531) plane on implantation and it can be due to the re-alignment of the grains as evidenced by our AFM measurement. AFM measurements also reveal the reduction in the grain size and the surface roughness on implantation. © *1999 Kluwer Academic Publishers*

1. Introduction

Studies on C_{60} have progressed rapidly in wide areas of science and technology because of its interesting and physical properties [1–3]. Solid C_{60} is an insulator having an optical absorption edge of about 1.6 eV [4]. Various groups have investigated the alkali metal doped C_{60} films whose physical properties range from insulator, semiconductor, metal to superconductor [5–7]. This can be achieved either by chemical doping or by ion implantation. Ion Implantation is technologically important in the fabrication of semiconductor devices requiring controlled dopant profiles. The major factors governing the successful exploitation of the ion implantation are the location and distribution of the implanted atoms inside the film, type and concentration of defects produced during implantation [8, 9].

Disintegration of C_{60} by heavy ion (Xe) irradiation resulting in the changes in electrical resistivity was investigated by Kalish *et al.* [10]. Kastner *et al.* [11] reported a change in sheet resistivity for K$^+$ ion implanted films only when the irradiation was carried out at temperature more than 300 °C. Compensation effects in C_{60} doped by 30 keV potassium ions were studied by Trouillas *et al.* [12]. They reported the possibility of n type doping with potassium ions. Field effect studies of thin films of C_{60} before and after implantation of potassium ions were also reported [13]. There are few reports in the direction of understanding the structural changes on ion implantation in C_{60} films using Raman and fourier transform infrared (FTIR) spectroscopies [14–16]. Isoda *et al.* [14] carried out Raman and FTIR measurements on the ion implanted C_{60} films and the studies revealed that for an implantation energy higher than 40 keV, C_{60} molecule itself disintegrates leading to a diamond like carbon structure. Implantation has also been found to change the wear and friction properties of C_{60} films [15]. It was found that the ion implantation

of 1×10^{16} Ar$^+$/cm^2 resulted in smoothening of the C_{60} films surface probably by compacting clusters, but without disintegrating the fullerene molecules. A high dose of 5×10^{16} Ar$^+$/cm^2 damaged fullerene molecules and converted into amorphous region as evidenced by their Raman and FTIR measurements. Misof *et al.* [17] reported the inbeam Mossbauer measurements on the iron irradiated fullerene films and they found that iron atoms occupied the interstitial positions. They also mentioned that crystalline peaks of C_{60} remained unchanged whereas the irradiation in C_{70} led to a fcc to rhombohedral phase transition. Proton irradiation in C_{60} films were investigated by Musket *et al.* [16] using glancing angle X-ray diffraction (GXRD), FTIR and low energy X-ray flourescence (LXRF) spectroscopies. The presence of broad FTIR bands and the absence of sharp diffraction peaks in GXRD revealed the transformation of crystalline to amorphous carbon. Apart from the changes in the transport properties, irradiation can induce structural changes. Many a times, changes in the transport properties could be traced to structural modification than to implantation itself. Hence studies on the structural properties of the irradiated film is essential.

Arsenic, being one of the most widely used semiconductor dopants was chosen for the present irradiation studies. In this paper, we present the structural investigations of As$^+$ implanted thin films. Both the pristine and implanted films were charecised by X-ray diffraction, atomic force microscopy and X-ray photoelectron spectroscopy. Our results on the changes in the electrical properties of the implanted films will be published elsewhere.

2. Experimental details

C_{60} thin films grown on Si (001) wafer by vacuum evaporation under a base pressure of 10^{-9} Torr using pure

C_{60} powder (99.98%). During film deposition, the substrate temperature was maintained at about 425 K. The thickness of the films was measured using Sloan Dek Tak Surface Profilometer and was found to be 100 nm. Mass analysed beam of 100 keV positive arsenic ions from a low energy accelerator was used for the implantation experiments.

Ion implantation was carried out at room temperature to various doses in the range 1×10^{13} to 1×10^{15} ions/cm^2. The beam current was maintained at about 0.5 microamperes to avoid local heating effect during implantation. The thickness of the films was measured using TRIM programme [18], the range of 100 keV arsenic ions in C_{60} is about 75 nm with a straggling of about 13.5 nm. This is smaller than the film thickness and hence it is expected that As$^+$ ion get implanted inside the film.
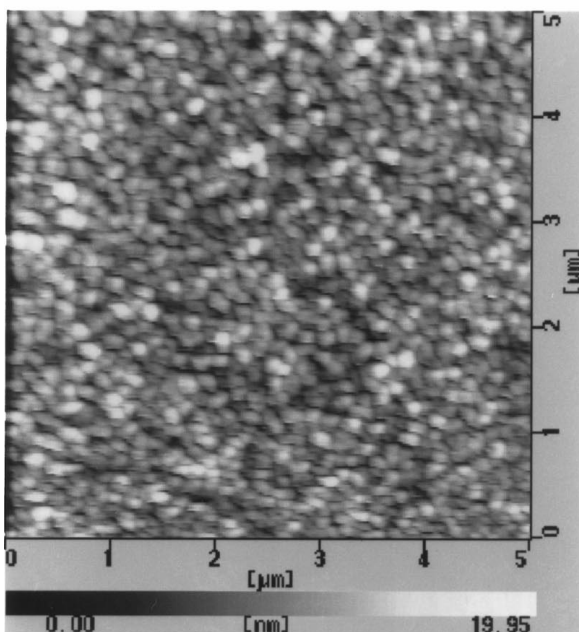
X-ray diffraction pattern of these films was recorded using a Rigaku X-ray diffractometer on the samples using CuK_α radiation. XRD data were collected in the 2θ range of 5 to 40° in steps of 0.02° with a dwell time of 20 s at each step. Grain morphology and the
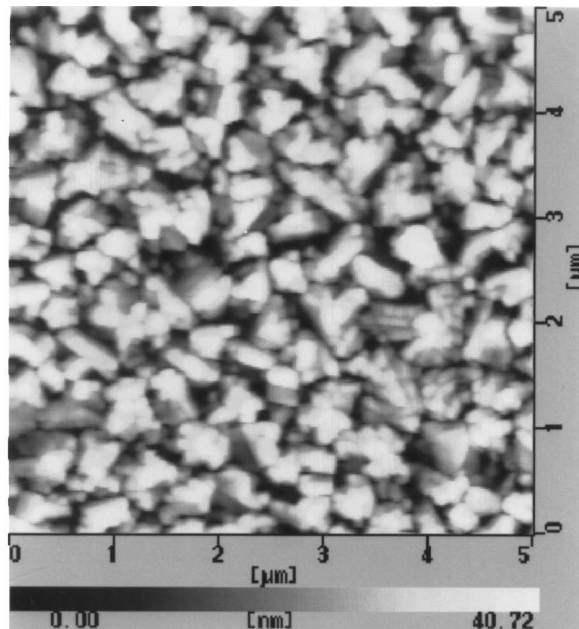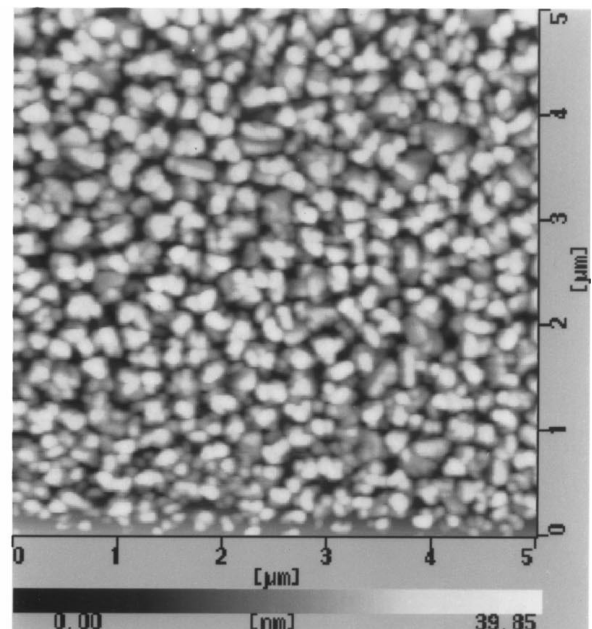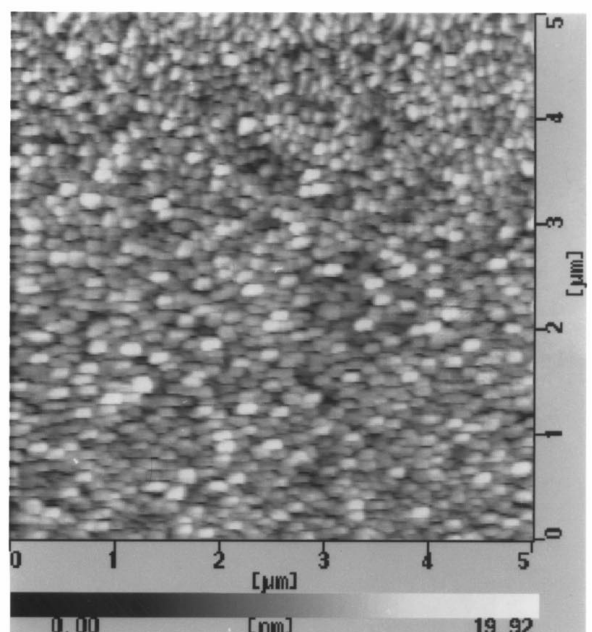

Figure 1 Atomic force micrographs of the as-deposited and films subjected to different doses of 100 keV positive arsenic ions. [Reduction in grain size is seen on implantation].

surface roughness were studied using the Seiko Instruments SPA 300 Atomic Force Microscope. XPS was employed to profile the implanted arsenic ions using PHI 5600 Multi Technic System and the X-ray target used was aluminium.

3. Results and discussion

Fig. 1 shows the AFM pictures of the as-deposited and implanted films. It is clearly seen that the grain size of the implanted films is smaller than that of pristine sample. Also, among implanted films the grain size decreases with the increase in the dose. Moreover, the intergrain connectivity which is poor in the case of as-deposited sample was found to improve with implantation. The surface roughness values were estimated as 8.25, 6.12, 4.60 and 4.64 nm for the as-deposited and 1×10^{13}, 1×10^{14}, 1×10^{15} ions/cm^2 respectively. From the X-ray diffraction patterns of the as-deposited and the implanted films (Fig. 2), it is seen that the films are polycrystalline. Relative intensities of the peaks of as-deposited thin films indicate that the film has a preferential orientation along (111) direction. On implantation, the intensity of the peaks in general is found to decrease accompanied by an increase in the background, especially at lower angles. Additionally, for the low implantation dose the (111) peak (at $2\theta = 10.8°$) of the unimplanted sample shifts to higher angle by 0.15°. A shift to higher angle of the same magnitude is also observed in the case of (2 2 2) peak on low dose implantation (1×10^{13} ions/cm^2). However other peaks undergo no shift on implantation. On high dose implantation (1×10^{15} ions/cm^2), the intensity of the (111) peak has completely vanished. Interestingly, the intensity of the peak at $2\theta = 37.84°$ which could be indexed as (531) of C_{60} fcc phase is found to enhance as the implantation fluence is increased.

Fig. 3 shows the XPS profile of the typically arsenic ion implanted film as a function of sputtering time. This sputtering time is directly proportional to the depth as measured from the free surface of the film. It is evident from the figure that no arsenic is found on the
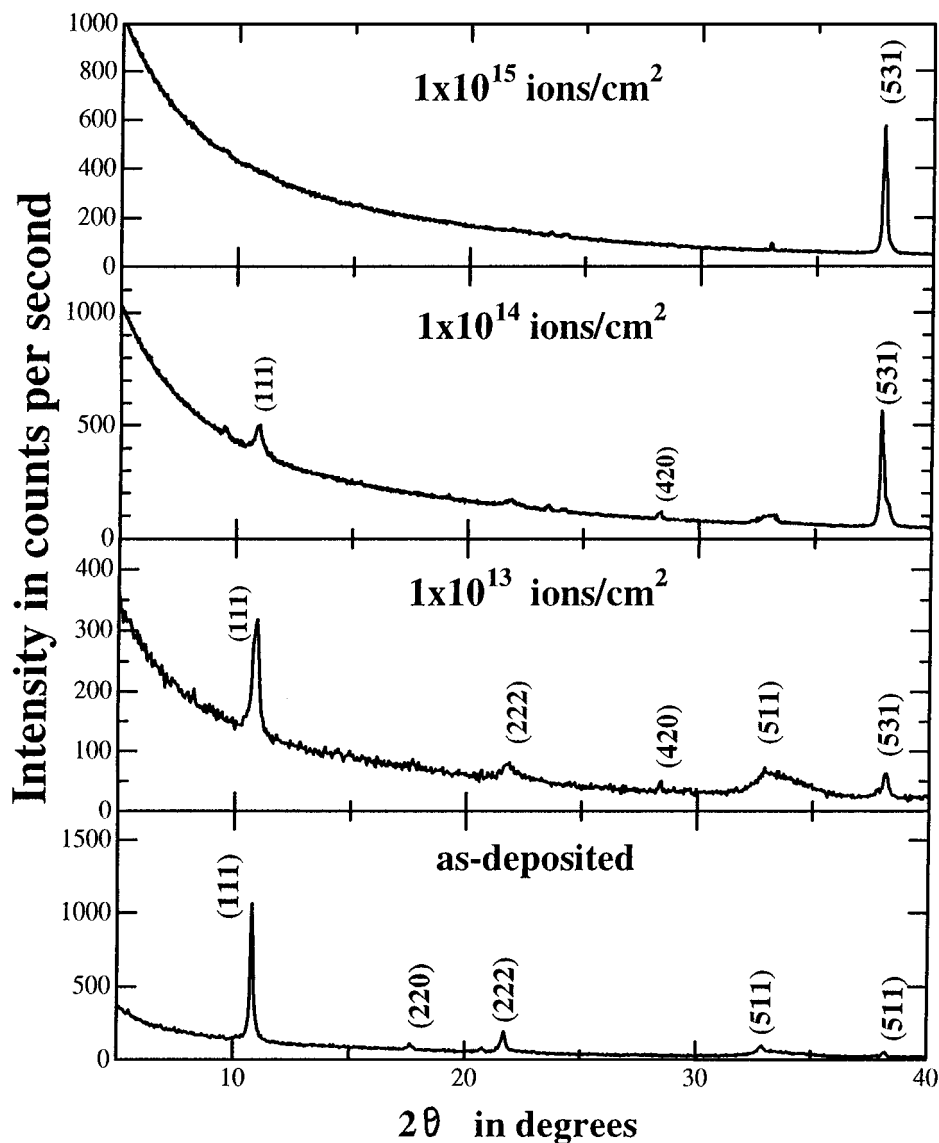
Figure 2 X-ray diffraction pattern of (a) as deposited thin film of C_{60} thin film coated on Si (001) wafer, (b) film subjected to a dose of 1×10^{13} ions/cm^2 arsenic ions at an energy of 100 keV, (c) film subjected to a dose of 1×10^{14} ions/cm^2 and (d) film subjected to a dose of 1×10^{15} ions/cm^2 [Preferred orientation along (531) plane is observed].
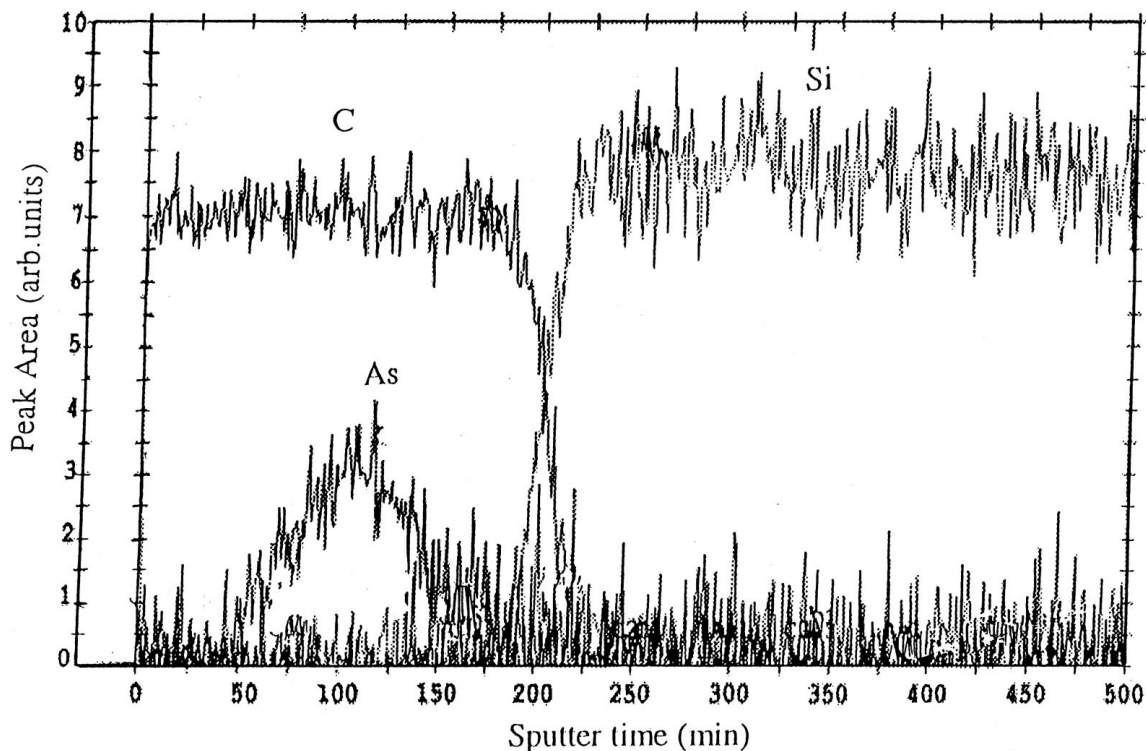
Figure 3 XPS spectra of the arsenic ion implanted film showing the formation of buried layer of arsenic within the fullerene thin film.

surface of the C_{60} film. It is also clearly seen that arsenic has not reached the silicon substrate during implantation to form any new compound. On the other hand, arsenic forms a buried layer within the fullerene film exhibiting nearly a symmetrical gaussian profile. The X-ray diffraction pattern of the as-deposited thin film of fullerene reveals the polycrystalline nature of the film with a preferred orientation along (111) direction. On implantation, there is no structural degradation or disintegration of the fullerene molecules observed. This in contrast to earlier observations where in loss of crystallinity as well as disintegration of the fullerene molecules were reported even at lower implantation energy, though for different implantation species [16]. As evident from Fig. 3, implantation of arsenic ions does not result in uniform doping but forms a buried layer of arsenic. This buried layer could induce strain within the film causing a shift in the peak positions of (111) and (222) peaks. The peak at $2\theta = 37.84°$ could not be assigned to known phase of arsenic. As the implanted arsenic had not reached the Si substrate, there could not be any intermixing of Si and As. Hence the peak should correspond to C_{60}. Also this peak could be indexed as (531) fcc phase of C_{60}. As could be clearly seen from AFM pictures (Fig. 2), that there is a reduction in the grain size with implantation doses. The grains with the reduction in their size upon implantation and under the strain induced due to buried layer of arsenic, may realign so as to increase the intergrain connectivity. This could also possibly lead to concommitant preferentially orientation of the grains along the (531) direction.

As no arsenic could be seen at the surface of the film, we believe that reduction in the surface roughness with implantation is a combined effect of realignment of the grains and preferential sputtering of the grains along

(111) direction. Increase in the background intensity of the X-ray diffraction patterns of the implanted films could be due to the ion implantation induced partial lattice damage, which is not unexpected.

4. Conclusion

Arsenic ion implanted thin films of fullerene were investigated by XRD, AFM and XPS to understand the structure of the films. XRD results reveal no loss in the crystalline nature of the film and no disintegration of the fullerene molecules upon implantation. Our XPS results establish that As forms a buried layer within the film causing strain within the film. It is argued that the combined effect of reduction in the grain size and strain within the film results in the reduction in the surface roughness as well as preferential orientation of the grains along (531) direction.

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