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High-energy He^+ ion beam induced modification in a-SiC:H

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The optical modification effect of high-energy (E=0.2-1.0 MeV) He^+ ion implantation in hydrogenated silicon-carbon alloy (a-$Si_{0.82}C_{0.18}$:H) films has been studied, using optical transmission, reflection and photo-thermal deflection spectroscopy (PDS) measurements in the near ultra-violet (UV) and visible range of the spectrum. As a result of the implantation, a well expressed “darkening” effect (i.e. absorption edge shift to the lower-photon-energy region) has been registered. It is accompanied by a remarkable increase in the absorption coefficient of over one order of magnitude, depending on the ion dose and energy. This change can be attributed to considerable He^+ ion beam induced structural transformations in the implanted hydrogenated silicon-carbon alloy films, as confirmed by additional Raman spectroscopy measurements.

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1. Introduction

Amorphous hydrogenated silicon carbide (a-$Si_{1-x}C_x$:H) alloy films have attracted much attention as structural materials for high temperature electronics and for various optoelectronic elements and devices operating in aggressive environments (acid vapors, radiation, open space, etc.) [1,2]. An important feature underpinning the material’s environmental robustness is the comparatively wide band gap which may be tailored in the range 1.8-3.0 eV [2].

The material can be prepared in thin film form on different substrates by chemical vapour deposition [3], or by a radio-frequency reactive magnetron sputtering method [4]. Mechanical, optical and electrical parameters of the material can be controllably varied by changing the relative composition of the constituent elements (x).

In addition, control of material properties can also be achieved using ion implantation [5,6]. Recently, using the emerging technology of ion micro-beams [7], promising results have been obtained for possible application of thin silicon carbide films in high-density optical data storage and sub-micron lithography [8,9]. This approach has been further developed by implementing ion doping with focused ion beam (FIB) systems that use Ga^+ or other chemically active ion species as implants [10-13].

In the present work, possibilities have been studied for applying focused high-energy (MeV range) ion implantation for the formation of optical contrast of suitable size to be used for optical data storage in a-$Si_{1-x}C_x$:H films. Initially, for this purpose broad beam high-energy He^+ ion implantation has been performed using a-$Si_{1-x}C_x$:H films with carbon content x=0.18. The implanted films have been studied using optical transmission, reflection and photo-thermal deflection spectroscopy (PDS) measurements in the near ultra-violet (UV) and visible ranges of the spectrum. Additionally, Raman spectroscopy measurements have been used to characterize the ion beam induced structural modification of the implanted material.

2. Experimental

Thin (d ~ 1μm) a-$Si_{1-x}C_x$:H films (x=0.18) were deposited onto Corning glass and polished silicon substrates for optical and IR measurements, respectively, by RF (13.56 MHz) reactive magnetron sputtering. A composite target, comprising a mono-crystalline (100) silicon wafer with chips of pure graphite placed on it, was sputtered in an Ar-20%H_2 gas mixture. Typical deposition conditions were: RF power 150 W (power density 1.91 W/cm^2), total gas pressure 1 Pa, substrate temperature 275°C, and graphite-to-silicon target ratio 0.025. The film thickness was determined by Talystep profilometry and conventional optical absorption measurements to be ~ 1 μm. Rutherford backscattering spectrometry was used to determine the carbon content, x, of the films.

High energy ion implantation of He^+ was performed at energies of 0.2, 0.5 and 1.0 MeV at room temperature and ion beam intensity 2-5 μA.cm^{-2}. Various ion doses were implanted in the range 1×10^{16} – 1×10^{17} cm^{-2}. A water cooling system for the sample holder was used to maintain room temperature during the implantation process.

PDS measurements were carried out in order to derive the absorption coefficient α in the photon energy range 0.6 - 3.8 eV. The Raman measurements were made with a

SPEX 1403 double spectrometer in photon counting mode, using the 488 nm excitation line of an Ar^+ laser.

3. Results and discussion

A considerable optical effect has been achieved in a-$Si_{1-x}C_x$:H films by high energy (E=0.5 MeV) implantation of He^+ for doses in the range 1×10^{16} – 1×10^{17} cm^{-2}. This effect is manifested by a transmission edge shift to larger wavelengths, accompanied by a decrease in the transmission coefficient as a result of the He^+ ion implantation. The optical absorption coefficient α shows a considerable increase, reaching over one order of magnitude for the longer wavelength range of the spectra, starting from the relatively low dose of 1×10^{16} cm^{-2} and quickly reaching saturation for the higher doses up to 1×10^{17} cm^{-2}, as demonstrated in Fig. 1.

The estimated ion range Rp for this high energy ion implantation (0.5 - 1 MeV) was above 2 μm [14], so well above the film thickness, allowing the main part of the ions and ion beam induced radiation defects (vacancies and interstitials) to be positioned in the glass substrate. Thus the main modification mechanism in the film itself, i.e. the absorption coefficient change, was defined by the electronic stopping of the ions in this area ($S_e = (dE/dx)_e$). This result clearly indicates that a-SiC:H forms defects from ionizing radiation. The process is efficient since there are more defects formed from the higher energy implants, where the electronic stopping term has been increased and nuclear collision damage is negligible. Note that whilst the mechanisms are different both electronic and nuclear collisions result in similar defects that modify the optical absorption [7]. Chemical effects have also been cited as the main mechanism in some cases [10].

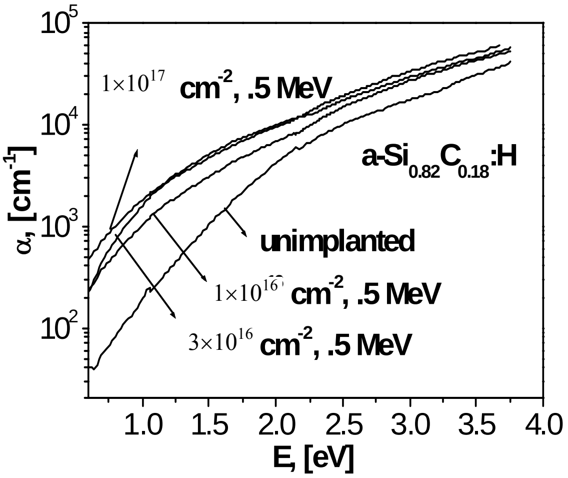


Fig. 1. Absorption coefficient α of un-implanted and He^+ implanted a-$Si_{0.82}C_{0.18}$:H films at an ion beam energy E = 0.5 MeV and different doses in the range 1×10^{16} – 1×10^{17} cm^{-2}.

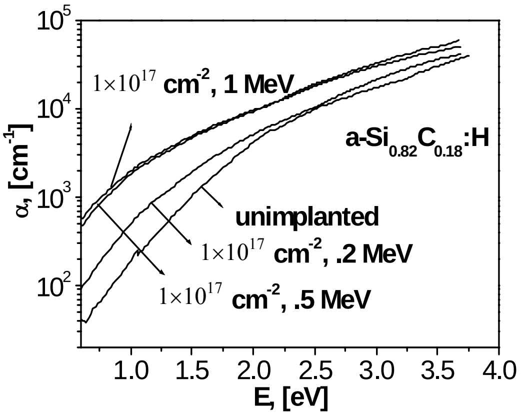


Fig. 2. Absorption coefficient α of un-implanted and He^+ implanted a-$Si_{0.82}C_{0.18}$:H films with an ion dose $D = 1\times10^{17}$ cm^{-2} and different energies in the range 0.2 – 1.0 MeV.

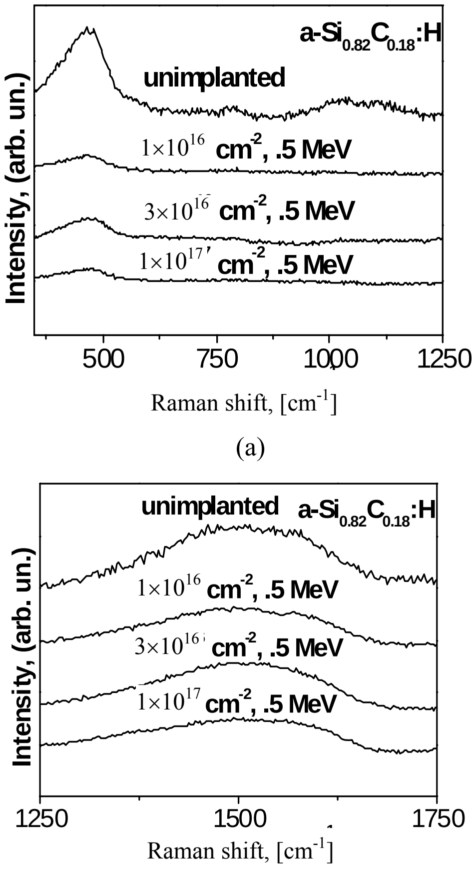
This is further confirmed by the results of the energy dependence for He^+ ion implanted a-$Si_{1-x}C_x$:H films at the highest dose D = 1×10^{17} cm^{-2} (Fig. 2). With the energy increase, from 0.2 MeV up to 1 MeV, the radiation defects for one and the same doses will penetrate even further into the Corning glass substrate and outside the silicon carbide film, leaving behind mainly the effects of the ion energy loss mechanism defined by the electronic stopping, i.e. the result of interaction of the energetic ions with the electronic systems of the host atoms (Si, C). Thus, the defects will change the bonding arrangements, and hence the energy band gap of the material therein, and related electronic parameters, such as the absorption coefficient α.

The results for the dose dependence of the Tauc optical gap E_g for the He^+ ion implanted a-$Si_{1-x}C_x$:H alloy films are shown in the Table 1. In the same table are presented the values of E_g for three different energies at the same dose; the results clearly showing the greatest E_g decrease for the highest ion energy (E = 1 MeV). The Urbach tail values show a decreasing tendency with both ion dose and energy. This is a clear indication for the increase of short range disorder.

Table 1. Tauc optical gap, E_g ,and Urbach tail values, E_o, of the un-implanted and He^+ implanted a-$Si_{0.82}C_{0.18}$:H films with different ion doses and ion beam energies.

Fluence, [cm^{-2}]	Energy, [MeV]	E_g, [eV]	E_0, [meV]
Unimpl.	0	2.08±0.01	226±2
1×10^{16}	0.5	1.67±0.01	232±2
3×10^{16}	0.5	1.63±0.01	280±2
1×10^{17}	0.2	1.74±0.01	252±2
1×10^{17}	0.5	1.59±0.01	284±2
1×10^{17}	1	1.36±0.01	286±2

The results of the Raman measurements (Figs. 3 and 4) give further evidence for the ion beam induced structural disorder in the implanted films. As seen, the Full Width at Half Maximum (FWHM) of the Si-Si TO-like peak at about 470 cm^{-1} already increases for the lowest dose (Fig. 3 a) while the peak intensity considerably decreases. A further dose increase at this energy does not result in additional noticeable changes in the spectra. When changing the energy of implantation (Fig. 4a), the FWHM of the same peak at ~ 470 cm^{-1} increases, while its intensity decreases again with the energy increase up to 0.5 MeV at the highest dose of implantation. Further increase of the energy at this dose does not cause additional changes in the spectra. These changes in the FWHM imply the introduction of increased disorder – an additional amorphisation of the films takes place during the implantation. In the higher energy region of the Raman spectra (Fig. 3 b and Fig. 4 b), the wide band corresponding to the C-C bonds in a-SiC:H films is present in the range 1250-1650 cm^{-1}. It comprises the bands at 1580 and 1380 cm^{-1} characteristic for polycrystalline graphite [15]. With increasing the ion energy up to 1 MeV for the highest dose case an increase is observed in the intensity of the lower energy band at about 1380 cm^{-1} which is related to the deterioration of the short range order in a-SiC:H films after high energy implantation with the highest dose (Fig. 4 b) [15].



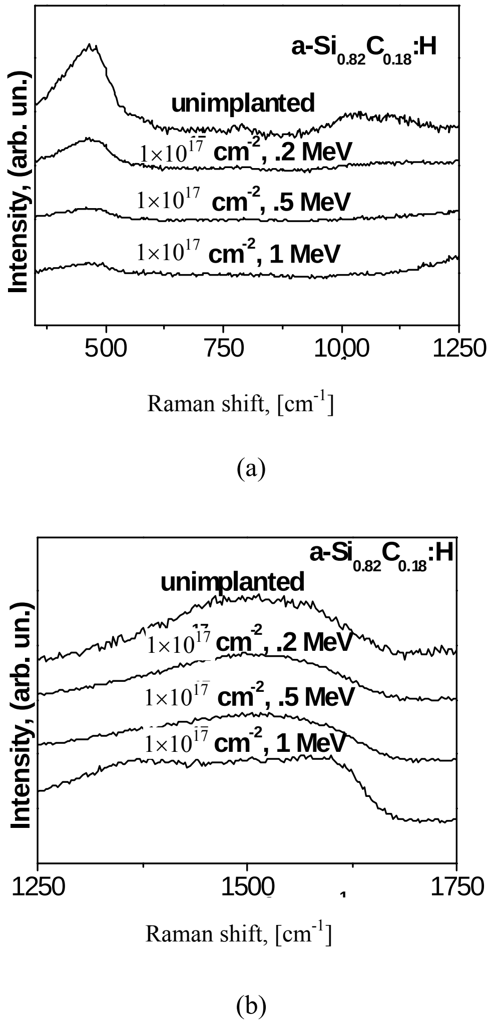
(a)

(b)

Fig. 3. Raman spectra of unimplanted and He^+ implanted a-$Si_{0.82}C_{0.18}$:H films at ion beam energy $E = 0.5$ MeV and different doses in the range $1{\times}10^{16} - 1{\times}10^{17}$ cm^{-2}, in the regions $350 \div 1250$ cm^{-1} (a) and $1250{\div}1750$ cm^{-1} (b).

4. Conclusion

High energy range He^+ ion implantation in a-$Si_{1-x}C_x$:H alloy films leads to observable optical modification of the implanted material. The formation of optical contrast in these materials has been achieved after He+ ion implantation with doses in the range 1 × 1016 – 1 × 1017 cm^{-2}, as demonstrated by the absorption edge shift and a considerable increase in the absorption coefficient α in the photon energy range 0.6-3.8 eV, reaching over one order of magnitude for the lower photon energy region. The obtained considerable changes in the optical properties of the He^+ ion implanted a-$Si_{1-x}C_x$:H alloy films could potentially be of interest in relation to the recently developed high-energy ion micro-beam technologies [16]. For further elucidation of the underlying mechanism of modification, additional experiments are underway.



(a)

(b)

Fig. 4. Raman spectra of un-implanted and He^+ implanted a-$Si_{0.82}C_{0.18}$:H films with ion dose $D = 1x10^{17}$ cm^{-2} and different energies in the range 0.2 – 1.0 MeV, in the regions $350 \div 1250$ cm^{-1} (a) and $1250{\div}1750$ cm^{-1} (b).

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