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Charge state dependent darkening in AsSe thin films induced by slow multiply charged Ne ions

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A charge state dependent effect of ion bombardment on the optical absorbance of AsSe thin films irradiated with 120 keV Ne^{q+} (q = 4...8) ions have been observed and traced back to the charge state dependence of the modified layer thickness and projected range of the ions. The projected range decreases by about 20 % with increase of the ion's initial charge state from 4 to 8. The elongation of charge equilibration for highly charged ions in a solid matter is discussed as a possible reason.

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How much does the range of highly or multiply charged ions in solids depends on the initial charge state (q) of the ion? To answer this question one should know how the stopping power depends on q and how long the charge equilibration processes last after the ion enters the solid. These questions have been matters of debate since the discovery of first ion sources capable of producing highly charged ions (HCI). In his pioneering work [1] Biersack, based on rather simplified theoretical estimations, concluded that though the stopping power moderately increases with the charge, the charge equilibration time is too short to affect significantly the range of a projectile having kinetic energy in the scope of importance for the semiconductor industry and for other applications (i.e. several tens or hundreds of keV). The experiments seemed to confirm this assumption [2]. Therefore, this view became rather common. Computer codes simulating ion penetration into solids usually treat the stopping power and the range of ions as a single valued function of the ion velocity [3]. Later a significant charge state dependence of the energy loss of slow HCI penetrating through thin carbon foils was experimentally demonstrated [4], also theoretical work appeared [3,5], which estimated the charge state dependence to be much stronger than previously thought. This has put the assumption of the insignificancy of the effect of the charge state on the ion range in doubt.

This work addresses this problem in an indirect way and to estimate the charge state dependence of the range of Ne^{q+} (q=4..8) ions in amorphous AsSe films through the effect of ion bombardment on the optical absorbance. This approach can be justified by the fact that the thickness of the damaged layer and the range of ions are closely related and almost identical [6-8].

It was shown in earlier works [9-11] that ion irradiation causes structural and optical changes in AsSe, As_2S_3 and other amorphous chalcogenides, similar to the well known changes induced by visible light exposure [12]. The most prominent of these changes is the redshift of the fundamental absorption edge, which is manifested as darkening i.e. transmittance decrease (absorbance increase) at wavelengths in the range of the Tauc's edge. Here we report the charge state dependence of this darkening induced by irradiation with multiply charged Ne^{q+} ions. The AsSe was chosen because its darkening is one of the largest, most reproducible and stable among binary chalkogenides.

The AsSe thin films were prepared by thermal evaporation of high purity AsSe glass onto oxide glass substrates in vacuum (the pressure of residual gases in the chamber was 2×10^{-5} mbar). In order to obtain uniformly thick films the substrates were mounted on a carrousel system and were rotated above the evaporation boat during the film preparation. The film thickness was 0.82 μm (it was measured with the help of an AMBIOS XP1 profilometer). The samples were cut into 1×1 cm^2 pieces and the transmittance spectra of each piece was measured in the 580 to 640 nm wavelength interval (with 1 nm steps) using a Shimadzu UV 3600 spectrophotometer. Then the pieces were mounted on a sample holder and irradiated with Ne^{q+} ions of different charge states and with different fluences. The irradiations were performed at the 14.5 GHz Electron Cyclotron Resonance Ion Source (ECRIS) of the Institute of Nuclear Research. The accelerating voltage was adjusted between 15 and 30 kV in order to set the kinetic energy of the ions to 120 keV for all q. This energy corresponds to the half of the Bohr velocity, i.e. falls into velocity range in which pre-equilibrium and charge state dependencies of the energy loss processes are expected to have most effect. At the same time this energy is sufficient to modify the target material deeply enough to cause easily measurable transmittance changes. SRIM [13] calculations gave

196 nm projected range with 116 nm straggling for 120 keV neon ions in amorphous AsSe.

After the irradiations the transmittance spectra of each sample was measured again. By dividing each spectrum obtained after irradiation by the corresponding spectrum measured before irradiation the relative change of the transmittance induced by the ion irradiation was obtained for each wavelength.

Selecting a particular wavelength and plotting the transmittance change against the ion fluence the kinetics of the ion induced darkening can be examined, the effect of ions with different initial charge states can be compared. A plot corresponding to 630 nm is shown in Fig. 1. Because of the few data points it does not say much about the details of the darkening process, but it clearly shows two important things: i) the transmittance decrease saturates at about 3-4×10^{14} ion/cm^2; ii) the saturation value of the relative transmittance change $(T/T_0)_{sat}$ depends on q.

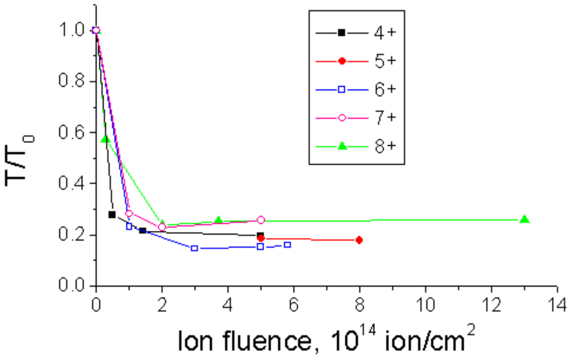

Fig. 1. The relative change of optical transmittance (measured at 630 nm) during irradiation with Ne ions of various charge states. The lines are guides for eyes.

Plots corresponding to other wavelengths look much the same, only the value of the $(T/T_0)_{sat}$ changes with the wavelengths. The relative values of $(T/T_0)_{sat}$ corresponding to different q, however, does not depend on wavelength. Fig. 2 shows the charge state dependence of $\ln(T/T_0)_{sat}$ normalized to the one corresponding to q=4 and averaged over the 580 to 640 nm wavelength interval. It provides a quantitative parameter for the characterization of the charge state dependence of the darkening, while its error (the dispersion of the normalized $\ln(T/T_0)_{sat}$ corresponding to different wavelengths) gives the amount of uncertainty caused by optical interference effects.

According to Beer's law

$$\ln\left(\frac{T}{T_0}\right)_{sat} = \ln r - \int_0^l \Delta\alpha(x)dx\,, \qquad (1)$$

where l is the thickness of the modified layer, $\Delta\alpha(x)$ is the depth distribution of the induced absorbance and $r = (1-R)/(1-R_0)$ accounts for the reflectance (R) change.

The $(T/T_0)_{sat}$ can be charge state dependent only if one or more of these three parameters is charge state dependent, as well. Let's examine them one by one. In principle, significant and charge state dependent sputtering also can cause this effect. To explore this possibility special measurements of possible sputtering have been performed, which supported the conclusion that at the fluences of our interest the irradiated film thickness change is comparable or less to the resolution of the profilometer (2 nm). So this possibility can be neglected.

The reflectance of as-prepared AsSe films is between 5 and 15 %, depending on the wavelength. Simultaneously with the darkening this value increases by 1 to 3 % [14]. To account for the observed charge state dependence of the $(T/T_0)_{sat}$ an approximately 16 % difference between the reflectance of Ne^{4+}- and Ne^{8+}-irradiated samples would be necessary. Thus, the contribution of r, if it is charge state dependent at all, is minor and in the first approximation can be neglected. Moreover, as the value of r is very close to 1 (between 0.96 and 0.99 as calculated from the above mentioned reflectance values), in further considerations we take r=1 and ln$r$=0 (in fact lnr = -0.01. -0.04, while $\ln(T/T_0)_{sat}$ =1.2 .. 3 depending on wavelength).

Obviously, this effect also cannot be the result of the charge state dependence of the $\Delta\alpha(x)$ alone. To notably affect the $(T/T_0)_{sat}$, the $\Delta\alpha(x)$ should be charge state dependent down to the rather significant depth. This automatically would mean that charge equilibration lasts rather long, which, through the higher stopping power for the ions of higher charge states, definitely would result in the simultaneous decrease of l and vice versa. The net effect of these two factors on the $(T/T_0)_{sat}$ is difficult to estimate. $(T/T_0)_{sat}$ increases with the decrease of l. Experiments with visible light and light ions [9-12] suggest that $\Delta\alpha$ slightly increases with the power density of exposition (i. e. the specific energy loss in the case of ions) until saturation at some power density. Thus, the change of $\Delta\alpha(x)$ is in the opposite direction to the change of l and hinders its effect to some extent. On the whole, as all this applies only to the rather thin top layer, the effect of charge state dependence of $\Delta\alpha(x)$ is very limited. Therefore, the charge state dependence of the $(T/T_0)_{sat}$ must be attributed to the charge state dependence of the thickness of the modified layer l.

Introducing effective values $\Delta\alpha_{eff}$ and l_{eff} instead of $\Delta\alpha(x)$ and l into equation (1) as $\Delta\alpha_{eff} l_{eff} = \int_0^l \Delta\alpha(x)dx$ we obtain a simple equation: $\ln(T/T_0)_{sat} = \Delta\alpha_{eff}\, l_{eff}$. Taking $\Delta\alpha_{eff}$, according to the above discussion, charge state independent, the normalized value of $\ln(T/T_0)_{sat}$ simply equals l_{eff}, i.e. Fig. 2 can be viewed as the charge state dependence of l_{eff}. Taking into account the strong correlation between the thickness of the modified layer and the ion's projected range, it means that the projected range is significantly charge state dependent.

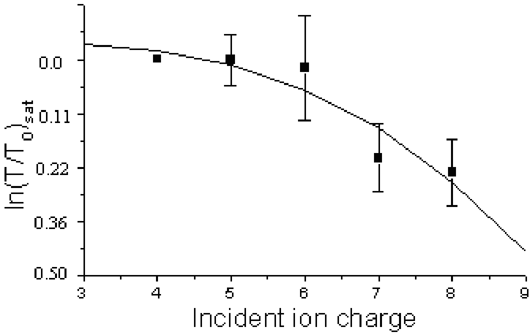

Fig. 2. The charge state dependence of the saturation values of relative transmittance changes. The solid line is the fit of eq. (2) (see the text).

The stopping of a highly charged ion in matter can be divided into two parts: stopping before and after charge equilibrium is reached. The pre-equilibrium stopping can be described by a pre-equilibrium stopping power $(dE/dx)_{pre}$ and a projected equilibration length Δx_{pre}. Both are functions of q. The further stopping is also characterized by an equilibrium stopping power $(dE/dx)_{eq}$ and a projected range Δx_{eq} corresponding to the ion energy after the charge equilibration. The sum of Δx_{pre} and Δx_{eq} gives the total projected range L. In order to estimate the charge state dependencies of $(dE/dx)_{pre}$ and Δx_{pre}, following the train of thoughts of Schenkel et.al. [4], we assume that they are simple power law functions of q: $(dE/dx)_{pre}=(\beta/\alpha)q^2$; $\Delta x_{pre}=\alpha q$. Taking into account that the equilibrium range is an approximately linear function of the projectile energy ($\Delta x=\gamma E$) [1], we obtain:

$$L = \gamma(E - \beta q^3) + \alpha q \qquad (2)$$

Tentatively assuming that $l_{eff}=\delta L$, where δ is a scaling factor (considering the strong correlation between the thickness of the modified layer and the projected range this is a fairly realistic assumption), we have fitted the data in Fig. 2 with eq. (2) to obtain the values of α and β. The value of γ was obtained from fitting the projected range data calculated by the SRIM code. Using these α and β values we have estimated $(dE/dx)_{pre}/(dE/dx)_{eq}=9.8\pm4.8$ and $\Delta x_{pre}=12.6\pm6$ nm, which are 3-5 times of values obtained by Schenkel et.al. [4] for stopping of gold ions in amorphous carbon foils. This difference may be attributed to the difference in physical properties of the amorphous carbon and amorphous AsSe: the first one is a half-metal, while the second one is a wide gap amorphous semiconductor, almost insulator.

In summary, the charge state dependence of the projected range of 120 keV Ne^{q+} ions (q=4...8) which penetrated amorphous AsSe films was confirmed by optical measurements of the resulting structural changes in this semiconductor material. The elongation of charge equilibration for highly charged ions in a solid matter can be the possible reason of the effect.

Acknowledgements

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