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DENSITY OF STATES MODIFICATIONS IN AMORPHOUS AND HYDROGENATED AMORPHOUS GERMANIUM AND THEIR EFFECT ON 3d CORE LEVELS BINDING ENERGY

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By using photoemission and partial yield spectroscopies the conduction band edge, the valence band and the 3d core levels of amorphous germanium hydrogenated and nonhydrogenated are studied and compared to that of crystalline Ge. We measure a 0.25 eV shift of the 3d core levels of amorphous Ge as compared to crystalline Ge whereas a smaller shift and a slight line - broadening are found in hydrogenated amorphous samples with low H content. These results are discussed in term of the contribution to the self energy due to relaxation of the valence electrons when a core hole is created.

The study of the electronic structure of tetrahedrally bonded amorphous semiconductors and their modifications induced by hydrogen incorporation is very important not only from the fundamental point of view, but also for the large technological interest of these hydrogenated semiconductors as solar cell devices. Photoemission studies of the valence bands have been extensively done both on Silicon and on Germanium showing strong similarities on the overall modifications induced by disorder as well as in the hydrogen induced features on the filled density of states. Recently it has been shown that disorder can effect core level too [1]. But, in contrast with the general agreement of the valence and conduction features, we find a different behaviour between the Si 2p and Ge 3d core levels. In fact while the 2p levels of Si show a large broadening with respect to the crystal and no change in the binding energy[1], the 3d levels of amorphous Germanium rigidly shift to lower binding energy with only slight broadening. The introduction of hydrogen in the amorphous matrix moves the levels back towards

higher binding energy with a shift dependent on the H concentration. In samples with low H content the binding energy of the 3d levels tends to assume the crystalline value whereas the linewidth is only slightly broadened. The difference in the valence and conduction density of states among crystalline, amorphous and hydrogenated amorphous germanium suggests that the 3d hole is differently screened by the valence electrons.

A core level analysis is carried out in order to correlate the observed shifts with the differencies in the density of states. The calculated contribution of the valence electron relaxiation to the core hole binding energy reproduces the observed trend and gives resonable numerical values.

Photoemission measurements were performed in a UHV-system ($p \simeq 1\ 10^{-10}$ Torr) by using the synchrotron radiation from Frascati ADONE storage ring. Details on exprimental apparatus are reported elsewhere[2]. Amorphous films ($\gtrsim 200$ Å) were evaporated in situ from a W-crucible onto a n-type ($n \sim 10^{17}\ cm^{-3}$) cleaved Ge(111)2X1 surface at room temperature. Hydrogenated amorphous films were prepared by proton bombardment of the growing Ge layer. By comparing the refractive index n=3.9 as extimated from our experimental data for low hydrogenated films with n_0 values reported in Ref. 3 as a function of H content, an hydrogen concentration $\gtrsim$ 5% has been inferred. Auger spectra did not show detectable presence of oxigen o carbon contaminants.

We show in Fig. 1 the Energy Distribution Curve (EDC), at $\hbar\omega$ =17 eV, of the valence bands of crystalline (c-Ge), amorphous (a-Ge) and hydrogenated amorphous Germanium (a-Ge:H). Two main disorder-induced modifications are observed[4,5] in the valence band of a-Ge which warrant the

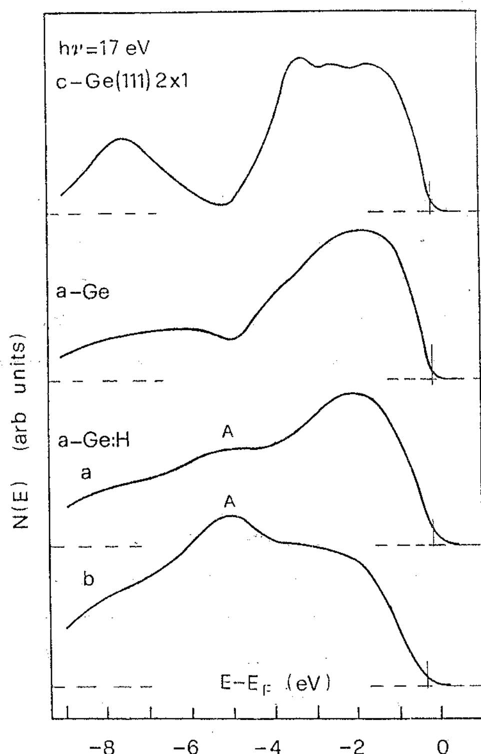

FIG. 1 - ECD's spectra of the valence band for c-Ge, a-Ge and two a-Ge:H films with law (a) and high (b) hydrogen content. The background of secondaries has been subtracted and the valence band maximum is indicated.

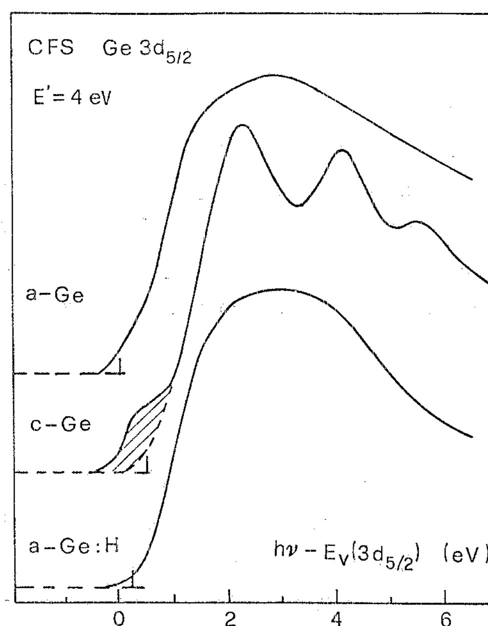

FIG. 2 - Constant final state (CFS) spectra for the Ge $3d_{5/2}$ level for c-Ge, a-Ge and a-Ge:H. The spectra, taken at an electron kinetic energy E'=4 eV, are normalized to the momochromator yield. The dashed area in the c-Ge curve is the surface state contribution. $E_V(3d_{5/2})$ is the binding energy of the $3d_{5/2}$ component measured from the top of the valence band.

amorphicity of the samples: i) an overall washing out of the structures and a partial filling of the gap between p and sp states; ii) a 0.5 eV shift toward lower binding energy of the center of gravity of the 3p states near the top of the valence band. In a-Ge:H the hydrogen introduction gives rise to a new structure at -5.2 eV (peak A in Fig. 1a and 1b). The magnitude of this peak which arises from sp bonding hybridization of Ge-H monohydrides[6,7] can be used to monitor the hydrogen content. A second hydrogen-induced effect is the state depletion at the top of the valence band which results in a shift towards higher binding energy of the first energy peak and in an increase of the pseudogap similar to what observed in a-Si:H[8]. As can be seen in Fig. 1, the effect increases with increasing H content.

The conduction band empty states measured by Partial Yield Spectroscopy from the $3d_{5/2}$ core level for c-Ge, a-Ge and a-Ge:H are shown in Fig. 2. The spectra are plotted versus $h\nu - E_V(3d_{5/2})$ i.e. by subtracting from the photon energy the binding energy of the $3d_{5/2}$ core level measured from the top of the valence band. Note that the absolute energy scale can be affected by excitronic effects[9,10]. A total resolution of ~ 0.5 eV results from the core hole lifetime (0.5 eV) and the monochromator resolution (0.1 eV). In the c-Ge curve the dashed area is the contribution due to empty surface states and the bulk structures at 2.2 eV, 4.0 eV and 5.6 eV, previously reported in Ref. 11, agree with theoretical calculation[12] and optical measurements[13]. The surface state peak is removed in a-Ge And replaced by a tail of states at the edge of the conduction band. The main structures of c-Ge are broadenend in a single peak centered at ~2.8 eV. The conduction band onset in a-Ge:H is sharpened by the effect of gap-states removal due to H. The remaining features of the conduction band appear to be independent of the H content.

The emission spectra of the 3d core levels have been measured on a large number of single crystals, amorphous films and hydrogenated amorphous films with different H concentrations. Fig. 3 summarize the results obtained. The upper three experimental curves have been fitted with two gaussian of equal width determined by the 3d hole lifetime (FWHM=0.5 eV in the crystal) and the experimental resolution (FWHM=0.45 eV). The spin-orbit splitting (Δ_{so}= 0.6 eV) and the branching ratio (BR=0.55) between the $3d_{3/2}$ and $3d_{5/2}$ components is also indicated in the figure. The 3d levels in a-Ge are found to be sistematically shifted to lower binding energy with respect to the crystal position by an average of 0.24±0.07 eV while the linewidth increases by 0.05 eV only. As

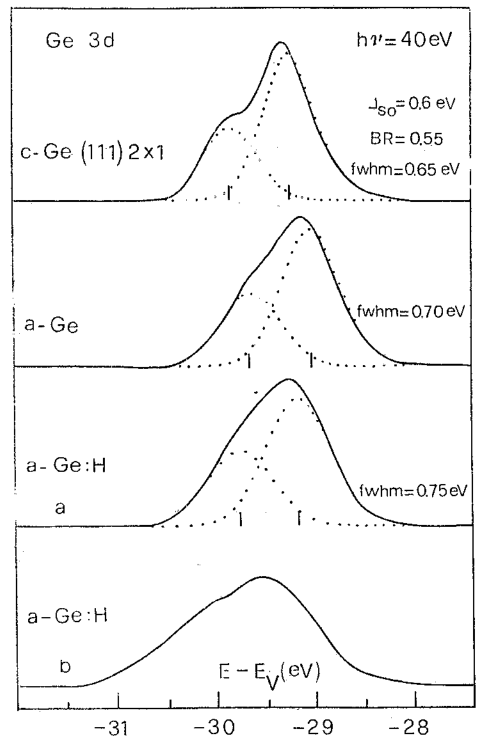

FIG. 3 - EDC's of the 3d core levels of c-Ge, a-Ge and a-Ge:H at 40 eV photon energy (solid line). The indicated values of the spin-orbit splitting Δ_{so} and branching ratio BR of the $3d_{3/2}$ and $3d_{5/2}$ components are obtained from the best fit of the experimental curve with two gaussians (dashed line) of equal width (FWHM). The binding energies are referred to the valence band maximum E_V.

mentioned previously, this behaviour of the 3d core levels in the transition from crystalline to amorphous Ge is found to differ markedly from that of Si 2p core levels, where no binding energy shift and a large lineshape broadening were observed[1]. In the a-Ge:H films both the 3d energy position and

the linewidth are a function of the hydrogen content. Similar energy shifts as a function of annealing and consequent variation of H amount have been reported in Ref. 14. Spectra a and b of Fig. 3 refer to a-Ge films respectively with low and high H content as confirmed by the corresponding valence bands of Fig. 1. In the samples with low H content (curve a) the core levels shift back towards the crystalline value and are positoned at 0.1 eV lower binding energy with respect to the crystal. When the amount of H increases, the levels shift to higher binding energy and broaden considerably (curve b). A fit of curve b with two gaussians would give a FWHM of 1.05 eV and a Δ_{so} of 0.8 eV, suggesting the presence of chemically shifted components on the high binding energy side of the curve arising from one or more H atoms bound to Ge atoms. This argument was proposed to explain the Si 2p core levels lineashape in a-Si:H[1]. We have attempted to interpret the energy shifts described above (except that for the very high H content which will be discussed in a subsequent paper) in terms of a change of the polarization self-energy Σ_p induced by the modifications of the valence and conduction band density of states. In fact, as it has been shown previously, one of the effects of disorder is to move the average density of valence and conduction states towards the gap region. This redistribution of states brings about a decrease of the effective Penn-gap[15] of the semiconductor. As a consequence one expects the screening of the valence electrons on a core hole to increase, lowering the binding energy of the level. The opposite happens when H is introduced in the amporphous matrix.

The binding energy of a core electron arises from the free atom contribution, the electrostatic field determined by the neighbouring atoms and rearrangements of outer electrons, and the relaxiation of the valence electrons when a core hole is created. We will make the hypotesis that the first two contributions are the same for the three different phases. This assumption seems reasonable since the first neighbour environment is conserved in c-Ge, a-Ge and a-Ge:H and the mean electronic valence density remains constant as indicated by the same experimental plasma frequency ($\hbar\omega_p$=16.6 eV) that we measured by Electron Energy Loss Spectroscopy. The largest term which contributes to the polarization self-energy Σ_p, within the approximation of a well localized core level separated from the upper valence band is given by[16]:

$$\Sigma_p = -\frac{1}{2}\int \frac{d^3q}{(2\pi)^3} V(q) \left\{ \frac{1}{\varepsilon(q)} - 1 \right\} \left| \int d^3r \left| u_c(r) \right|^2 e^{iq.r} \right|^2$$

where $V(q)=4\pi e^2/q^2$ is the Fourier transform of the Coulomb potential, $u_c(r)$ is the core wave function[17] and,

$$\varepsilon(q) = 1 + \frac{\left(\frac{\hbar\omega_p}{\hbar\omega_g}\right)^2 . F}{\left(1 + \frac{E_F}{\hbar\omega_g} F^{1/2} \frac{q^2}{K_F^2}\right)^2}$$

with $F=1-(\hbar\omega_g/4 E_F)$ is the interpolation formula of the dielectric function in the Penn's model[15]. The values of the Penn gap $\hbar\omega_g$ have been evaluated from the approximated expression of the static dielectric constant $\varepsilon_o= 1+(\hbar\omega_p/\hbar\omega_g)^2 F$. ε_o for a-Ge and a-Ge:H was derived using the sum rule $\varepsilon_o= 1+(2/\pi)\int_o^{\infty} d\omega' \varepsilon_2(\omega')/\omega'$, where $\varepsilon_2(\omega)$ is the imaginary part of the dielectric function. For crystalline and amorphous germanium ε_2 is known from optical measurements[18,19]. The ε_2 spectrum for a-Ge:H

can be calculated using the non direct transition model:

$$\varepsilon_2(\omega) \propto \frac{|M_{cv}(\omega)|^2}{\omega^2} \int_0^{\infty} d\omega' \, \varrho_v(\omega'-\omega) \, \varrho_c(\omega')$$

where ϱ_v and ϱ_c are the experimental density of states reported in Figs. 1, 2 and the matrix elments $M_{cv}(\omega)$ are desumed from optical measurements[18] of $\varepsilon_2(\omega)$ for amorphous germanium with the assumption that they are the same in a-Ge:H. The values obtained for ε_o are 15.6 for c-Ge, 18.5 for a-Ge and 15.5 for a-Ge:H, in good agreement with the values reported in the literature[3,18]. Equation (1) gives for Σ_p 7.98 eV, 8.11 eV and 7.96 eV, i.e. an energy shift towards lower binding energy of 0.13 eV between c-Ge and a-Ge and of 0.15 towards higher binding energy between a-Ge and a-Ge:H. The calculated values of Σ_p are plotted in Fig. 4 vs. ε_o. The two experimental points refer to the

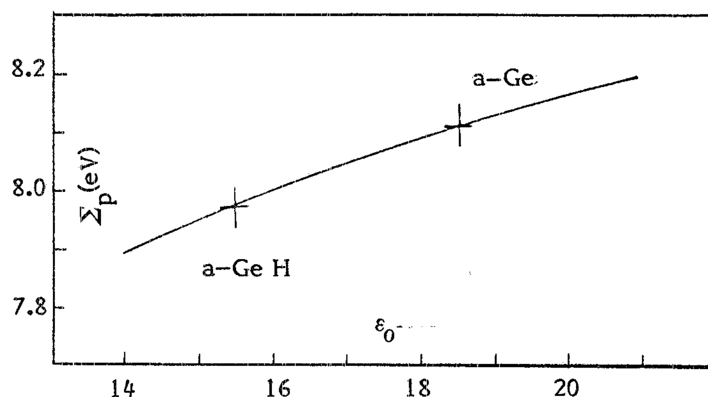

FIG. 4 - Calculated values of the polarization self-energy Σ_p versus ε_o. The two experimental points correspond to the measured shift between the 3d levels of the a-Ge and a-Ge:H films (see Fig. 3).

measured shift between a-Ge and a-Ge:H. It can be concluded that this analysis reproduces the experimental trend and gives a numerical value of the core levels shift between a-Ge and a-Ge:H In agreement with the measured values. A lower agreement is found between the crystalline and the two disordered systems. The reason for this behaviour can be two-fold: i) the inadequacy of the Penn's model in describing simultaneously a crystalline and an amorphous solid[20], ii) long range disorder induced variations in the electrostatic field in the amorphous systems which have been neglected in the binding energy shift considerations.

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