Core Excitons in Amorphous Semiconductors

F. Evangelisti,[a] F. Patella,[b] R. A. Riedel, and G. Margaritondo[c]
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

and

P. Fiorini
Dipartimento di Fisica, Università "La Sapienza", I-00185 Roma, Italy

and

P. Perfetti and C. Quaresima
Istituto di Struttura della Materia, I-00044 Frascati, Italy

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Core excitonic effects at the $L_{2,3}$ absorption edge were investigated with a combination of optical and synchrotron-radiation photoemission techniques in crystalline, amorphous, and amorphous-hydrogenated silicon and silicon-carbon alloys. Our results support a Frenkel-type nature of these excitons.

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Core excitons in crystalline semiconductors have been the subject of a long debate.[1–5] In many cases, the binding energies are at least one order of magnitude larger than those of the valence excitons.[3,4] This enhancement cannot be explained by effective-mass theoretical models.[3] Hjalmarson, Büttner, and Dow[4] proposed that the central-cell interaction could produce a localized exciton similar to a Frenkel exciton, incompatible with effective-mass theories. Strinati[2] emphasized that the relaxation of the electronic states around the excited electron–core hole pair is incomplete, and therefore the dynamic screening of their interaction is reduced. This enhances the excitonic binding energy of the Frenkel-type excitons.[4] This effect increases when the average electron-hole distance decreases. Following a different theoretical approach, Zunger[5] also predicted that the localization of the excited electron near the core hole enhances the exciton binding energy. We present here evidence that the $L_{2,3}$ core excitonic binding energy is large in amorphous silicon systems and that it appears to increase with the degree of disorder. Since the excited-electron localization also increases with the degree of disorder, our results are consistent with the common prediction of the above theories.[2,5] And they support in general a Frenkel nature of the Si $2p$ exciton.

The experiments were performed on five kinds of materials: crystalline silicon (c-Si), amorphous silicon (a-Si), and hydrogenated amorphous silicon (a-Si:H) and silicon-carbon alloys (a-Si$_{1-x}$C$_x$:H) with or without B doping. The c-Si surfaces were obtained by cleavage in ultrahigh vacuum. The a-Si films were obtained *in situ* by electron-beam evaporation. The a-Si:H and silicon-carbon alloys were grown by rf glow discharge and cleaned by Ar-ion sputtering (possible effects of H depletion were tested by sputtering in a mixture of H and Ar and were ruled out). The C-Si alloy composition was determined by Auger spectroscopy. The H content of the hydrogenated samples was investigated by infrared spectroscopy and found to be ~10%. The joint density of states in the gap region of all hydrogenated samples was investigated by combining optical absorption measurements with the spectral dependence of the photoconductivity.[6] The distance in energy E_{2p} between the Si $2p$ core level and the top of the valence band, E_v, was deduced from photoelectron energy distribution curves (EDC's) taken in the valence band and Si $2p$ regions at photon energies $h\nu = 40$ and 135 eV with full width at half maximum (FWHM) resolution of 0.2 and 0.65 eV. The position in energy of the $L_{2,3}$ edge, $E_{L_{2,3}}$, was obtained from partial-yield (PY) photoemission spectra[7,8] taken at two different photoelectron kinetic energies, $E_k = 1$ and 4 eV, with resolution of 0.35 eV. Because of lifetime broadening, excitonic lines are not resolved at the $L_{2,3}$ edge. Experimental evidence for core excitonic effects is provided by the steepness of the edge line shape and by the discrepancy between the optical gap E_g and the "photoemission gap" $E_{\mathrm{pg}} = E_{L_{2,3}} - E_{2p}$ which gives an estimate of the core exciton binding energy, $E_{\mathrm{ex}} = E_g - E_{\mathrm{pg}}$. The forbidden gap was estimated from optical absorption spectra $\alpha(h\nu)$ such as those shown in Fig. 1 for our hydrogenated samples. E_g is given[9] by the extrapolation to zero of the square-

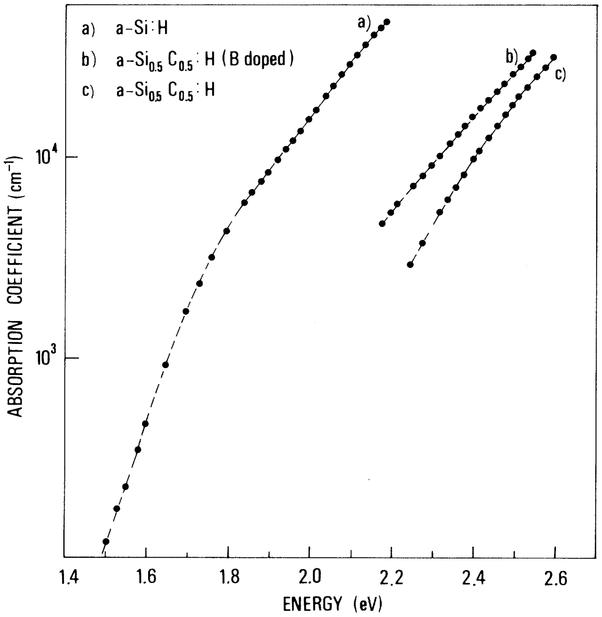

FIG. 1. Optical absorption coefficient in the near-gap region of our hydrogenated amorphous samples.

root dependence of α, and the results are shown in Table I. Also shown in Table I are the values of E_4, the energy at which $\alpha = 10^4$ cm^{-1}. This value of α roughly corresponds to 10^{20}–10^{21} states cm^{-3} eV^{-1} and to the onset of the transitions between states near the mobility gap.[10] Because of the steepness of $\alpha(h\nu)$, it is reasonable to take either E_4 or E_g as a measure of the forbidden gap—the small discrepancy does not affect our conclusions.

Si $2p$ EDC's and $L_{2,3}$ PY curves are shown in Fig. 2 and the corresponding peak positions E_{2p} are reported in Table I. The line shape of the c-Si EDC is determined by the Si $2p$ spin-orbit doublet structure. This broadened doublet line shape is smeared out for a-Si by the valence-charge fluctuations due to bond-length and bond-angle variations,[11] which leave the overall linewidth essentially unchanged. The hydrogenation of a-Si introduces new components in the Si $2p$ spectrum due to Si atoms bound to one or more H atoms and it gives rise to the asymmetric high-energy tail of the Si $2p$ peak.[11] The majority of the Si atoms, however, still have four-silicon-atom coordination. This explains why the peak position and the slope of the low-energy side for the a-Si:H spectrum remain unchanged with respect to a-Si. A large shift of the peak and a broadening of both sides can be seen instead for the a-Si$_{0.5}$C$_{0.5}$:H spectrum. The presence of a large fraction of C atoms introduces a strong compositional disorder with a variety of configurations for the Si nearest neighbors, corresponding to a multiplicity of chemical shifts. The Si $2p$ line shape is determined by the envelope of the corresponding spectral components. Therefore the Si $2p$ line shape and in particular its linewidth Δ_{2p} (see Table I) is a probe of the increasing disorder from mainly topological in a-Si, to topological with a small compositional component in a-Si:H, and finally to topological with a large compositional component in the Si-C alloys.

Structure smearing and broadening by disorder are also visible in the $L_{2,3}$ PY curves of Fig. 2(b).

TABLE I. Values in electronvolts deduced from our data. E_{2p} is the Si $2p$ binding energy referred to the top of the valence band. $E_{L_{2,3}}$ is the position of the $L_{2,3}$ absorption edge. E_g is the optical gap. E_4 is the energy at which $\alpha = 10^4$ cm^{-1} (another estimate of the gap). E_{pg} is the photoemission gap (see text). The difference between E_{pg} and E_g is emphasized by the apparent gap reduction, $1 - E_{\text{pg}}/E_g$. The last column gives the difference $E_{\text{ex}} = E_g - E_{\text{pg}}$. Also given are the widths Δ_{2p} and $\Delta_{L_{2,3}}$ of the Si $2p$ peak and of the $L_{2,3}$ edge.

	E_{2p} (± 0.1)	Δ_{2p}	$E_{L_{2,3}}$ (± 0.1)	$\Delta_{L_{2,3}}$	E_{pg} (± 0.2)	E_g	E_4	Apparent gap reduction (%)	E_{ex}
c-Si	98.85 (centroid) 98.7 ($2p_{3/2}$)	1.2	99.7 (L_2)	0.3[a]	1.0	1.12	· · ·	11	0.12
a-Si	99.0	1.2	99.6	0.5	0.6	1.26[b]	1.4[b]	52	0.66
a-Si:H	98.95	1.6	99.75	0.6	0.8	1.75	1.95	54	0.95
a-Si$_{0.5}$C$_{0.5}$:H	99.8	2.1	100.15	1.0	0.35	2.2	2.4	85	1.85
a-Si$_{0.5}$C$_{0.5}$:H, B-doped	99.7	2.45	100.25	0.9	0.55	2.05	2.3	73	1.5

[a] Width of the L_3 edge.

[b] From Ref. 9.

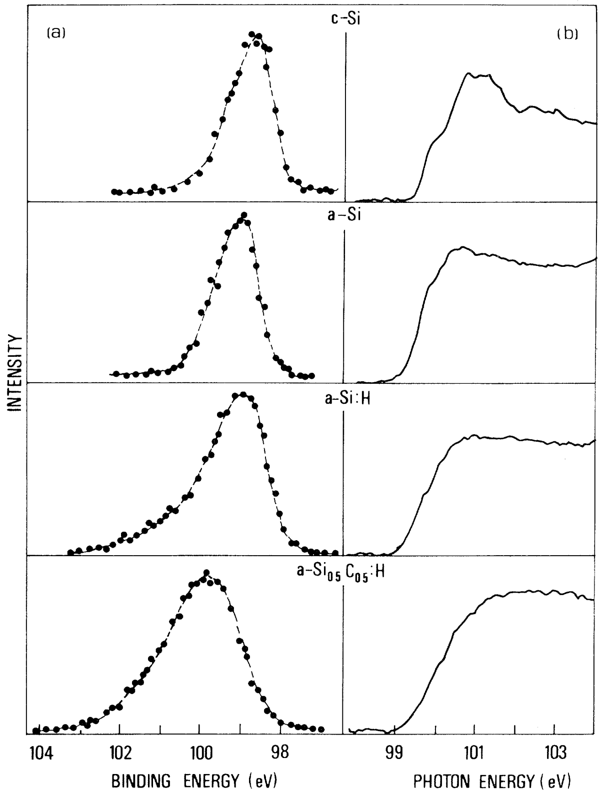

FIG. 2. (a) Si $2p$ photoelectron energy distribution curves (EDC's) taken at a photon energy $h\nu = 135$ eV. The binding energy scales are referred to the top of the valence band. (b) $L_{2,3}$ absorption edges measured in the partial-yield mode of photoemission.

From the point of maximum slope of these curves we deduced the edge positions $E_{L_{2,3}}$ and the values of E_{pg} shown in Table I together with the edge width $\Delta_{L_{2,3}}$.[12] Notice that $\Delta_{L_{2,3}}$ is always significantly smaller than Δ_{2p}, a steepness indicative of many-body effects. The discrepancy between E_g (or E_4) and E_{pg} dramatically increases with increasing disorder on going from *c*-Si to *a*-Si and to the hydrogenated samples (this fact is emphasized by the "apparent gap reduction," $1 - E_{\mathrm{pg}}/E_g$, shown in Table I). For *a*-Si$_{0.5}$C$_{0.5}$:H, in particular, the value of E_{pg} would correspond to a hypothetic conduction-band edge well below the position of the Fermi level. Similar effects were recently found in preliminary experiments performed on amorphous and hydrogenated-amorphous Ge and Ge-Si alloys.[13]

We carefully analyzed possible spurious factors affecting $E_{\mathrm{ex}} = E_g - E_{\mathrm{pg}}$. Extrinsic localized gap states could affect the estimate of E_v by linear extrapolation of the valence-band EDC's leading spectral edge, which merges into the noise at a signal level 0.05–0.1 times the intensity of the highest-in-energy valence-band Si $3p$ feature. Since this feature is produced by $\sim 2\times10^{22}$ states cm^{-3} eV^{-1},[14] our E_v corresponds to $\sim 10^{21}$ states cm^{-3} eV^{-1}, large enough to guarantee that it is determined by states of intrinsic nature. Furthermore, our E_v's correspond to a constant value $E_{2p} = 99.0 \pm 0.1$ eV for different *a*-Si and *a*-Si:H samples—while this value would change from sample to sample if E_v was affected by extrinsic states. Finally, the measured valence-band discontinuities for *a*-Si and *a*-Si:H films on our substrates[15,16] were never larger than 0.1–0.2 eV which gives an upper uncertainty limit for the influence of extrinsic gap states on the deduced E_v's and E_{2p}'s. A similar analysis can be applied to the onset of core-to-conduction-band transitions measured in the PY photoemission mode, deducing a similarly small uncertainty for $E_{L_{2,3}}$. The typical overall uncertainty for E_{ex} is 0.2–0.35 eV for our amorphous materials, i.e., slightly larger than for *c*-Si but still not large enough to affect our conclusions.[17] The apparent conflict of previously published results made the above careful analysis necessary. Early suggestions of important *a*-Si $L_{2,3}$ core excitonic effects were made by Brown, Bachrach, and Skibowski[18] and recent values of E_{pg} reported by Reichardt, Ley, and Johnson[19] are in excellent agreement with ours. Wesner and Eberhardt,[20] however, reported larger values $E_{\mathrm{pg}} = 1.3$ and 1.6 eV for sputtered *a*-Si and *a*-Si:H. Although the causes of the discrepancy between those values and ours are not clear at present, the sample preparation procedure may play an important role by influencing the degree of disorder.

Our large E_{ex}'s and Si $L_{2,3}$ edge widths smaller than the core-hole widths are two effects explained by a reduced screening of the electron-hole interaction.[2,5] The increase of E_{ex} from sample to sample could be explained in part, following the approach of Ref. 4, with the fact that a Frenkel-type exciton is not pinned to the bottom of the conduction band, E_c. We found E_c to move to higher energies as E_g increases on going from *c*-Si to *a*-Si, to *a*-Si:H, and to the Si-C alloys, and this could enhance E_{ex}. The theoretically predicted role of the screening suggests that this effect combines with those of the increased disorder in determining the measured enhancements of E_{ex}. For example, a disorder reasonable for *a*-Si would be sufficient to enhance E_{ex} by localization. The localization parameter[21,22] is not easy to estimate in real systems, but ~ 10 Å is reasonable for states 0.2–0.3 eV near the mobility edge of *a*-Si.[22] A linear-combination-of-atomicorbitals cluster calculation by Ching and Lin[23] deduced a "localization" (with meaning somewhat different from the formal theories[21,22] and not directly related to the Anderson localization) of the order of 3–4 Å for the electrons in the states near the band edges of *a*-Si. From the results of Ref. 23 we deduce a density of localized final states of the order of 10^{21} cm^{-3}, roughly corresponding to the experimental absorption edge.

In conclusion, our results support a Frenkel-type nature of the Si 2*p* excitons. An upper limit for E_{ex} in a molecular exciton is given by molecular Si compounds. Values of 2–5 eV have been found for the lowest levels of the Rydberg series in gas-phase SiH_4[24] and SiF_4 and in solid SiH_4.[25] The binding energies up to 1.85 eV found in the present study are not far from those limits.

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[a] Permanent address: Dipartimento di Fisica, Università "La Sapienza," 00185 Roma, Italy.

[b] Permanent address: Dipartimento di Fisica, Università di Tor-Vergata, Roma, Italy.

[c] Author to whom all correspondence should be addressed.

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