Photoinduced Optical Absorption in Amorphous Si_xGe_{1-x}:H

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A transient optical absorption has been observed at low temperatures in amorphous Si_xGe_{1-x}:H excited by laser. The temperature and laser-intensity dependences were found to be similar to those observed for the photoinduced ESR signal seen in amorphous Si:H and Ge:H. It is shown that most characteristics of the induced absorption can be described in terms of the polaron theory.

We report the first observation of a transient photoinduced optical absorption band in amorphous $(a\text{-})Si_xGe_{1-x}$:H. It bears some striking similarities and important dissimilarities with the metastable photoinduced band in chalcogenide glasses[1]; its characteristics also resemble those of optically induced paramagnetic resonance seen in a-Ge:H[2] and a-Si:H.[3] We show that at Ge-rich alloy compositions the position and shape of the band agree with the results of simple calculations based on the polaron model.

Photoinduced absorption was observed in samples of a-Si_xGe_{1-x}:H $(0.17 < x < 1.0)$ obtained from three different laboratories. We used 1–1.5-μm-thick films of amorphous Si and Si-Ge alloys deposited on sapphire substrates by glow-discharge decomposition of a gaseous SiH_4/GeH_4 mixture, and films of a-Si sputtered in an argon-hydrogen atmosphere. One sputtered sample was on a roughened c-Si substrate and was about 14 μm thick. The optical properties of these films have been described elsewhere.[4,5]

The samples were placed in a liquid nitrogen cryostat and illuminated by an Ar^+ laser $(\lambda = 514.5$ nm) chopped at 160 Hz at power densities up to ~ 5 W/cm^2. Suitably filtered light from a 650-W tungsten lamp was used as the probe beam in the spectral region 0.25–1.8 eV. The transmitted probe light was analyzed by a monochromator and its modulation ΔT was synchronously detected. This was always 180° out of phase with the excitation, indicating that absorption was induced in the films. A correction was made for the luminescence spectrum in those samples which exhibited photoluminescence.

All samples showed some photoinduced absorption at liquid-nitrogen temperature. The peak transmission change $\Delta T/T$ showed little variation from sample to sample and no trend with alloy composition: At 120 K, $-\Delta T/T$ was in the range of 10^{-4} to 10^{-3} and corresponded to $\Delta \alpha \sim 5$–50 cm^{-1}. Interference fringes were prominent in the $\Delta T/T$ spectra of the thin films; it can

be shown that this is an expected result of a small induced absorption. The fringes were averaged in the normalized spectra shown in Fig. 1; the energy resolution is limited to one fringe spacing, typically 0.06–0.11 eV.

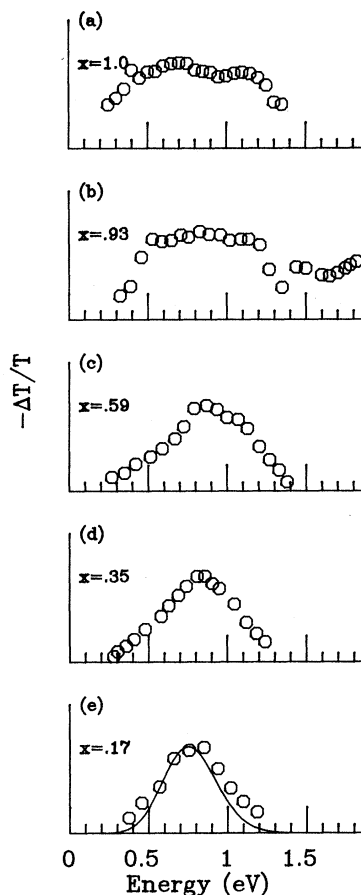In Si-rich alloys, a broad band which is possi-

FIG. 1. Normalized spectra of induced absorption, $-\Delta T/T$, in a-Si_xGe_{1-x}:H at 120 K. The sample in (a) is a 14 μm sputtered film; (b)–(e) are thin films (1 to 1.5 μm) deposited by glow discharge. In (e), the solid line is the theoretical absorption calculated for electron-like small polarons.

bly a superposition of two peaks is seen between 0.2 and 1.5 eV. With increasing Ge content, the spectrum narrows to a band with a peak at 0.85 eV and a half-width of 0.5 eV [points in Fig. 1(e)]. The high-energy increase in $\Delta T/T$ in Fig. 1(b) is probably due to a downward shift of the absorption edge induced by heating.

The temperature dependence of the induced absorption at 0.56 eV in the sputtered sample of Fig. 1(a) is shown in Fig. 2. At high temperatures, the absorption strength decreases with an activation energy of 0.10 eV. For temperatures below about 130 K the absorption becomes more weakly dependent on temperature. The dependence of $\Delta T/T$ on the laser intensity I_L was measured for the same sample at $\hbar\omega = 0.56$ eV and $T = 120$ K. We find $\Delta\alpha \sim I_L^{1/2}$ within experimental error in the range of laser photon flux 10^{17}–10^{19} cm^{-2} sec^{-1}.

The same measurements were made on the Ge-rich sample of Fig. 1(e) at $\hbar\omega = 0.86$ eV. The temperature dependence was similar but the variation of induced absorption with laser intensity was weaker and could be fit to either $\Delta\alpha \sim I_L^{1/3}$ or $\Delta\alpha \sim \ln I_L$; the latter dependence could be due to saturation of the absorbing centers in the thin layer where the laser light is strongly absorbed.

Intraband free-carrier absorption can immediately be ruled out as an explanation of our data, since this is expected to produce absorption mon-
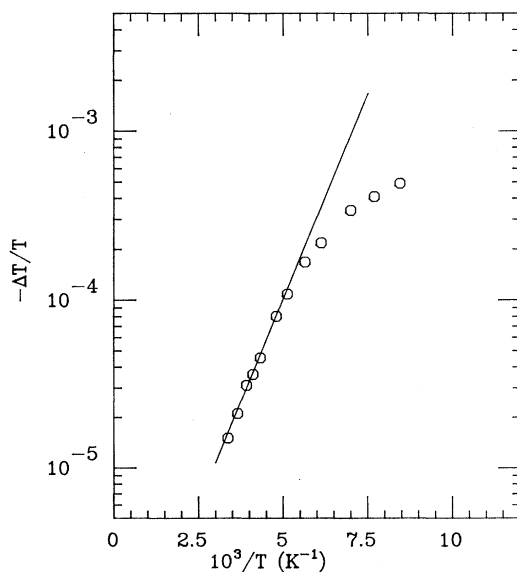
otonically increasing with decreasing photon energy. Neither can the prevailing interpretation of the metastable photoinduced absorption seen in many semiconducting chalcogenide glasses[6-8] explain the spectra of Fig. 1. In that model, carriers are thought to be trapped at charged defects and can then be photoionized into the bands; but this mechanism (transition from a discrete level to a quasicontinuum) is expected to produce absorption increasing monotonically with photon energy. This prediction is in accord with the observations in chalcogenide materials over the experimentally accessible spectral range, but contrasts with the data reported here. The peaked spectrum of induced absorption in a-Si$_x$Ge$_{1-x}$:H is evidence for a mechanism of resonant transitions of photocarriers which does not involve states in the bands.

It has also been suggested[9] that the induced absorption and ESR seen in chalcogenides is due to the presence of small-radius polarons formed when the photoexcited carriers are self-trapped by lattice distortion. The optical properties of polarons have been discussed by several authors[10] and have been invoked to explain sub–band-gap absorption in various low-mobility materials with excess carriers introduced by doping[11] or optical injection.[12] In this mechanism, incident light induces the polaron to hop to an adjacent site with photon absorption and simultaneous phonon emission; the polaron energy change is zero. At low temperatures this process produces an absorption band peaked at roughly four times the height of the barier to phonon-assisted hopping E_H. The band has a width of $8\,(E_H\hbar\omega_0/2)^{1/2}$, where ω_0 is the average frequency of optical phonons involved in polaron formation. If carriers of both signs form polarons two peaks should occur, but the absorption strength of the less mobile polaron is reduced by the dc mobility ratio.

In Fig. 1(e) the normalized theoretical absorption band[13] of electronlike polarons in pure a-Ge:H is plotted and compared with the data on a Ge-rich sample. This is based on the TO-phonon energy (0.035 eV) measured by vibrational spectroscopy[14] and a hopping activation energy (0.2 eV) obtained from a study[15] of the temperature dependence of dc conductivity and thermopower in a-Ge:H whose behavior is consistent with polaron formation. The close correspondence of the theoretical and experimental curves is remarkable in view of the fact that no fitted parameters were used.

The induced absorption spectrum of alloys with

FIG. 2. Temperature dependence of induced absorption at 0.56 eV in sputtered a-Si:H sample of Fig. 1(a). High-temperature activation energy is 0.10 eV.

higher Si content cannot be interpreted as a single polaron band because the broadening is too large to be accounted for by the increase in TO-phonon energy in going from a-Ge to a-Si, which should increase the width of the band by a factor of only $(\omega_{Si}/\omega_{Ge})^{1/2} \sim 1.3$. It is more likely that a second peak at higher energies is superimposed with a possible electron-polaron band centered at 0.7–0.85 eV. There is evidence[16-18] that in a-Si:H holes are self-trapped with a hopping activation energy of 0.2–0.4 eV; in a polaron model they would produce an absorption band in this spectral region.

Localized electronic states of nonpolaronic origin (possibly defect related) probably exist in the pseudogap of these materials and could also produce a resonant-induced absorption if they have a ground state above the equilibrium Fermi level and at least one bound excited state. A large linewidth would be expected either from disorder or from lattice distortion about the site, as in color-center absorption. In an amorphous solid, the latter mechanism of absorption is not sharply distinct from that involving polaron hopping, because in both processes the lattice relaxation which follows electronic excitation lowers the electron's energy and changes the spatial distribution of its (localized) wave function to a greater or lesser degree. The magnitude of the relaxation effects, however, does not influence the absorption spectrum although it has important bearing on transport and thermal properties.

A lower limit for the induced density of absorbing centers can be obtained from $\Delta\alpha$ with the assumption that the upper limit to the absorption cross section is given by the cross section for an isolated defect with unity oscillator strength.[19] This gives a range of 6×10^{15} to 2×10^{16} cm^{-3} for the alloys, using a peak $\Delta\alpha$ of 10 cm^{-1}. By comparison, the saturated spin density found in transient photoinduced ESR measurements in a-Si:H (Ref. 3) and a-Ge:H (Ref. 2) is 10^{16}–10^{17} cm^{-3}.

The transient character of the induced absorption and ESR in a-Si$_x$Ge$_{1-x}$:H contrasts sharply with the photoinduced effects in chalcogenide glasses, which are long lived. The theoretical lifetime of an electron-hole polaron pair in a-As$_2$Se$_3$ has been calculated to be[9] $\sim 10^3$ sec; assuming a polaron hypothesis and using the parameters given above for the band in a-Ge, this time comes out to $\sim 10^{-5}$ sec. A decay time of this order is consistent with our observations. Weaker effective electron-phonon coupling in germanium is responsible for the difference.

The temperature and intensity dependence results give information about the recombination processes of polarons or other absorbing centers. We infer from the intensity dependence $\Delta\alpha \sim I_L^{1/2}$ that recombination kinetics are bimolecular, and hence the density, N, of induced centers in the steady state is $N = (G/b)^{1/2}$, where G is the optical generation rate and b is the bimolecular recombination coefficient, $dN/dt = G - bN^2$. The change of $\Delta\alpha$ with temperature is therefore governed by b $(\Delta\alpha \sim b^{-1/2})$, where b is proportional to the mobility of the more mobile carrier. For polarons or otherwise localized carriers this has the high-temperature form $\mu \sim \mu_0 \exp(-E_H/kT)$ and then becomes weakly temperature dependent at low T where phonon-assisted hopping is ineffective. The behavior shown in Fig. 2 is consistent with this model and, in addition, the slope of the activated portion of the curve (0.10 eV $\sim E_H/2$) is very close to one-eighth the energy of the induced absorption peak (0.7–0.85 eV $\sim 4E_H$) as it should be for polarons. The calculated upper limit for b is 3×10^{-10} cm^3 sec^{-1}.

Photoinduced ESR in a-Si:H is observed[2] to have the same temperature and intensity dependence as we find for induced absorption, indicating that similar states are responsible for both effects. Recent photoluminescence measurements[18] also find bimolecular recombination at high intensities, where the excess carrier density is estimated to exceed 10^{18} cm^{-3}. Comparison with our earlier estimate of the density of absorbing centers then indicates that either the transitions we observe have a low oscillator strength or that not all carriers participate in the absorption.

The properties of the induced absorption in a-Si$_x$Ge$_{1-x}$:H show some qualitative similarities to the results of photoinduced ESR and luminescence experiments. A group of similar optically induced effects seen in chalcogenide glasses are thought to have a common origin involving localized states in the gap. Whether this is the case in a-Si and a-Ge is not yet clear. Our results indicate that induced absorption spectroscopy can provide information complementary to that obtained from photoinduced ESR and luminescence, and is therefore a useful probe of the detailed nature of the electronic states in these materials.

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