Effect of oxygen on the optoelectronic properties of amorphous hydrogenated silicon

B. G. Yacobi, R. W. Collins, G. Moddel, P. Viktorovitch,* and W. Paul

Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

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Experimental observations of the effect of a small percentage (1.6−5.7 at. %) of deliberately incorporated oxygen on various properties of sputtered a-Si:H reveal a broadening of the absorption edge, an increase in the density of states near the Fermi level (determined from capacitance and conductance measurements), an increase in the photoelectron mobility-lifetime product $(\mu\tau)_n$, a decrease in the photohole $(\mu\tau)_p$ product, and a widening of the photoluminescence peak. These are accompanied by the appearance of a Si-O vibrational mode in the infrared spectra at about 1000 cm^{-1}. We also report apparently the first observation of photoluminescence in sputtered a-Si:O $(C_O = 55$ at. %). The above results are self-consistently interpreted in terms of a suggested modification of the gap density of states in a-Si. It is confirmed that the incorporation of oxygen at the 1 at. % level into a-Si:H is detrimental to the photovoltaic performance of the material.

INTRODUCTION

The principal effects on the optical and electronic properties of a-Si of the passivation of defects by hydrogen are now well established.[1] Incorporation of oxygen at the 1 at. % level in sputtered a-Si:H has been shown to lead to a significant increase in the photoconductivity, a decrease in the conductivity activation energy, and the appearance of a Si-O vibrational mode in the infrared spectra.[2] In an extension of this study to higher oxygen contents in glow-discharge deposited a-Si:H, Knights et al.[3,4] have found a quenching of the photoluminescence (PL),[5] an increase in the full width at half maximum (FWHM) of the PL peak, and an increase in the dangling-bond spin density. Delahoy and Griffith have observed a slight deterioration in the photovoltaic conversion efficiency of a-Si:H solar cells with the introduction of oxygen into the SiH$_4$ plasma during the film deposition.[6] Significant differences in the effects of oxygen on the infrared vibrational absorption, ESR, and photoconductivity, depending on whether the oxygen is incorporated during the deposition or by diffusion after the growth of the film, have also been reported.[7−9]

In an extension of our earlier studies designed to obtain a better understanding of oxygen-induced modification of the basic properties and those pertinent to solar cells, we present results of the effects of deliberate incorporation of a few atomic percent oxygen on the mobility-lifetime products of both the electrons $(\mu\tau)_n$ and holes $(\mu\tau)_p$, the gap density of states (DOS) near the Fermi level, the optical absorption in the visible, the infrared vibrational spectra, and the temperature dependence of the photoluminescence, in addition to the properties reported previously.[2] We suggest a schematic model of the effect of oxygen incorporation on the gap DOS, which is consistent with the data currently available on this system. We also report apparently the first observation of PL in sputtered a-Si:O which contains no H but approximately equal amounts of Si and O.

EXPERIMENTAL

A full description of the preparation of sputtered a-Si:H in this laboratory is given elsewhere.[7] For the films prepared for this study the base-vacuum pressure was less than 5×10^{-7} Torr. The partial pressure of argon was kept at 5×10^{-3} Torr, with the partial pressures of hydrogen and oxygen maintained at constant values in the ranges of $(0.2−2) \times 10^{-3}$ and $(0.01−0.06) \times 10^{-3}$ Torr, respectively. The substrate temperature, which was calibrated by an a-Ge thin-film bolometer placed on the platform during the film deposition, was held at 200 °C. The deposition rate was about 1 Å/sec and films were simultaneously deposited on a variety of substrates for the different measurements. For the unhydrogenated a-Si:O films the partial pressure of oxygen was kept at 0.2×10^{-3} Torr and the substrate temperature was held at 350 °C.

TABLE I. Results of measurements on a-Si:O:H: the hydrogen concentration C_H derived from the Si:H wagging vibrational mode at 640 cm^{-1}, the oxygen concentration C_O measured by electron microprobe, E_{04} and E_{03}, the photon energies at which α is equal to 10^4 and 10^3 cm^{-1}, respectively, the density of states (DOS) near the Fermi level derived from the capacitance and conductance measurements of Schottky devices, full width at half maximum (FWHM) of the photoluminescence (PL) peak at 77 K, PL peak position E_{PL}, relative PL intensity I_{PL}, the mobility-lifetime product of holes $(\mu\tau)_p$ derived from the spectral dependence of the short-circuit current of Schottky devices, and the photoelectron $(\mu\tau)_n$ derived from measurements of the photoconductivity.

C_H (at. %)	C_O (at. %)	E_{04} (eV)	E_{03} (eV)	DOS (cm^{3}eV^{-1})	FWHM (eV)	E_{PL} (eV)	I_{PL} (rel.)	$(\mu\tau)_p$ (cm^{2}V^{-1})	$(\mu\tau)_n$ (cm^{2}V^{-1})
7	0	1.74	1.54	5×10^{17}	0.31	1.12	0.06	2×10^{-10}	1×10^{-8}
7	1.6	1.77	1.55	2×10^{18}	0.36	1.17	0.06	1×10^{-11}	7×10^{-8}
14	0	2.10	1.89	3×10^{16}	0.32	1.49	1.0	5×10^{-9}	5×10^{-9}
14	4.3	2.17	1.92	7×10^{16}	0.37	1.48	0.43	5×10^{-10}	4×10^{-8}
14	5.7	2.17	1.93	7×10^{17}	0.37	1.49	0.32		9×10^{-8}

Details of the measurements of the optical absorption in the visible[10] and infrared,[11] the derivation of the low-energy optical absorption from the spectral dependence of photoconductivity,[12] and the measurement of PL (Ref. 13) have been given elsewhere. Capacitance and conductance measurements of Schottky devices with Pt electrodes were used[14,15] to derive the DOS near the Fermi level. These devices were used to derive the mobility-lifetime product of holes $(\mu\tau)_p$, from the spectral dependence of the short-circuit current.[16] The photoelectron $(\mu\tau)_n$ was determined from photoconductivity measurements with coplanar electrodes.[17] The oxygen contents of our films were measured by an electron microprobe using a wavelength dispersive spectrometer. The absolute accuracy of these measurements is approximately 5%.

RESULTS AND DISCUSSION

The results are summarized in Table I. First we will consider the results of the infrared absorption measurements. Figure 1 shows the absorption spectra of a-Si:O:H between 500 and 1200 cm^{-1}. The integrated area under the absorption band centered at 640 cm^{-1}, which is the characteristic Si-H wagging vibrational mode, was used to estimate the hydrogen content.[18,19] The oxygen-related feature in this range is the mode at 950 cm^{-1} (curve A, dashed line) which is shifted to about 1000 cm^{-1} with increased oxygen content (curves B and C). Other features at 790 and 820 cm^{-1} observed for high concentrations of oxygen also result from oxygen-related vibrational modes, the exact nature of which is difficult to determine. The infrared

spectra for high hydrogen content films ($C_H=14$ at. %) exhibit also the Si-H$_2$ bending mode at 890 cm^{-1} (curves B and C).[22] No O-H stretching vibration, which would appear at 3700 cm^{-1}, was observed in our films.

The integrated optical-absorption coefficient of the Si-O mode at 1000 cm^{-1}, obtained from the deconvoluted spectrum, has been correlated with the oxygen concentrations derived from our microprobe measurements with the result that

$$C_O(\text{at. \%})=0.25 \int \alpha d(\hbar\omega) \text{ at. \% cm/eV },$$

where C_O is the oxygen concentration[23] and $\hbar\omega$ is
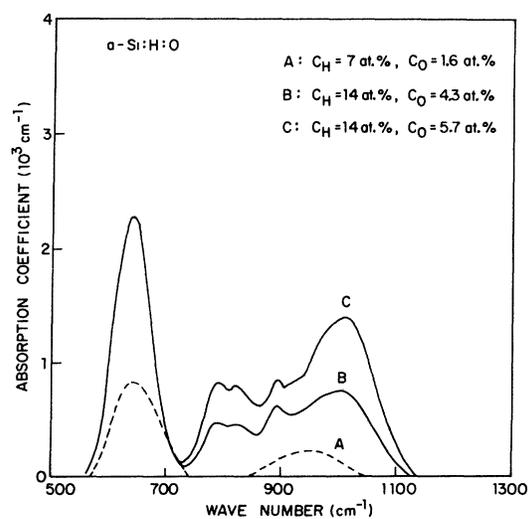
FIG. 1. Infrared absorption spectra of a-Si:O:H. Curve A (dashed line) is for the sample with $C_H=7$ at. % and $C_O=1.6$ at. %. Curves B and C are for films with $C_H=14$ at. % in both cases and with C_O of 4.3 and 5.7 at. %, respectively.
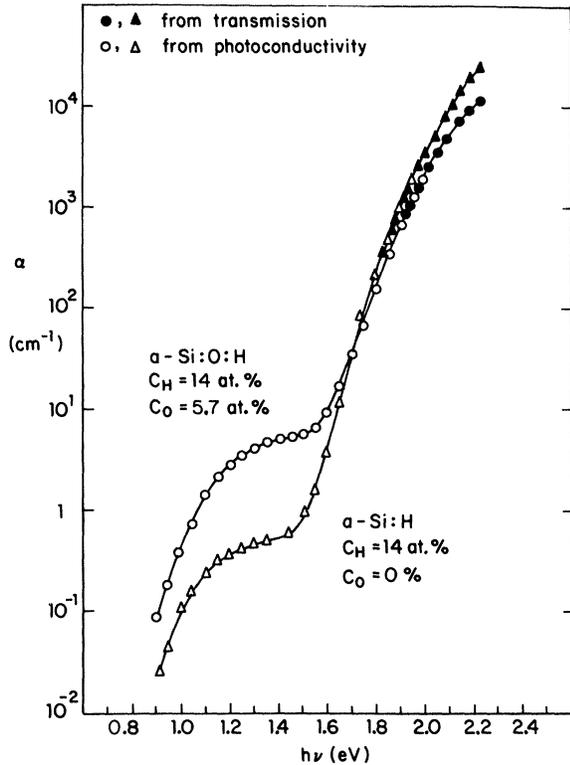
FIG. 2. Optical-absorption coefficient α versus photon energy $h\nu$ for a-Si:H (triangles) and a-Si:O:H (circles). $C_H = 14$ at. % in both cases and $C_O = 5.7$ at. % for a-Si:O:H. The α versus $h\nu$ dependence was obtained from optical transmission measurements extended by photoconductivity.

the photon energy. A similar correlation for the crystalline silicon-oxygen compound gives the preintegral factor of 0.06,[24] which means that the oscillator strength of the Si-O vibration is significantly decreased in a-Si:O:H as compared to the crystalline case.

We now consider the effect of oxygen on the DOS and optoelectronic properties of a-Si:O:H. Figure 2 shows the absorption coefficient α versus photon energy $h\nu$ for a-Si:H and a-Si:O:H, with $C_H = 14$ at. % in both cases and $C_O = 5.7$ at. % in the a-Si:O:H. A distinct shoulder below about 1.5 eV is clearly visible in both cases. Several transitions that may give rise to the absorption around 1.2 eV have been considered previously and it was demonstrated[12] that those most likely to produce this absorption in a-Si:H are from the gap states just below the Fermi level to the conduction band. It seems reasonable to extend this interpretation to a-Si:O:H. In the range of about $(1.6-1.8)$ eV the absorption edges can be described by the exponen-

tial dependence $\alpha(h\nu) \propto \exp(h\nu/E_\alpha)$. It has been suggested that the exponential slope results from the energy dependence of the density of states in the valence-band tail,[25] in which case the broadening of the absorption edge in a-Si:O:H, shown in Fig. 2, indicates a broadening of that tail. This is accompanied by an increase in E_{04}, shown in Table I.

The results of measurements of the temperature dependence of the PL in a-Si:H, a-Si:O:H, and a-Si:O are presented in Fig. 3. The temperature dependence of the photoluminescence can be expressed as

$$I(T) = I_0 \frac{p_r(T)}{p_r(T) + p_{nr}(T)}$$

where p_r and p_{nr} are the radiative and nonradiative recombination probabilities.[26] By plotting $\ln\{[I_0/I(T)] - 1\}$ as a function of temperature, p_{nr}/p_r was shown to obey the relation $p_{nr}/p_r \propto \exp(T/T_0)$, where T_0 is a characteristic temperature which depends on the slope of the DOS at the conduction-band edge.[27] The larger T_0 for oxygenated samples indicates an increase in the width of the conduction-band tail. This is consistent with the increase in the FWHM of the PL peak shown in Table I.[28]

The direction of change of the PL efficiency with
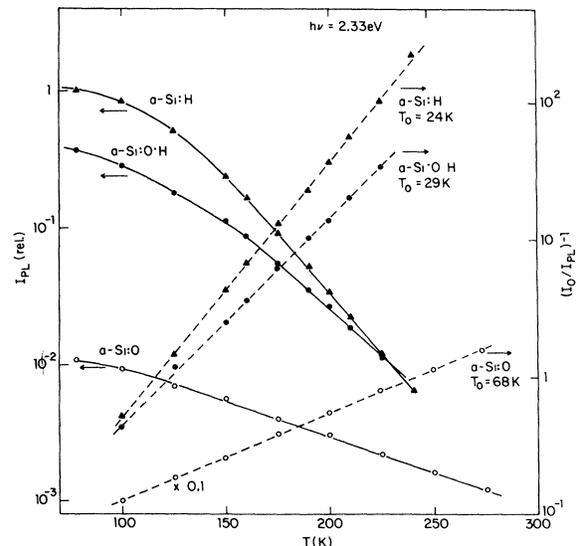
FIG. 3. Temperature dependence of the PL intensity for a-Si:H and a-Si:O:H ($C_H = 14$ at. % for both cases, and $C_O = 5.7$ at. % in a-Si:O:H) and for a-Si:O ($C_O = 55$ at. %) (solid lines), and $\ln[(I_0/I) - 1]$ versus T for the same samples (dashed lines). The excitation energy of the PL is 2.33 eV.
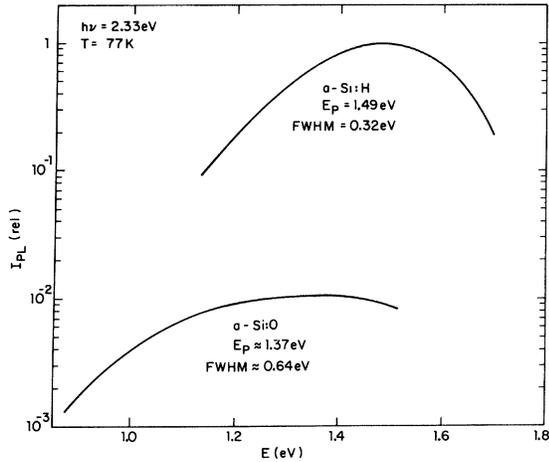
FIG. 4. Typical PL spectrum of sputtered a-Si:H and PL spectrum of a-Si:O. The excitation energy of the PL is 2.33 eV.

DENSITY OF STATES

FIG. 5. Schematic model of suggested dependence of the density of states (DOS) for a-Si, a-Si:H, and a-Si:O:H. For simplicity, no sharp features are presented in the DOS, since the proposed explanation of the results does not deal with their exact position and shape.

oxygenation in a-Si depends on the degree of hydrogenation: (i) In a film with neither H nor O, no PL is observable,[13] whereas in an unhydrogenated a-Si:O film with $C_O = 55$ at. % (no evidence of H in the infrared spectrum), the PL is significant. As can be seen from Fig. 4, the PL exhibits a broad band (FWHM = 0.64 eV) with $T_0 = 68$ K (see Fig. 3), indicative of broadened band tails. This compensation of defects in a-Si, evident from the significant PL efficiency, is consistent with the reduction of the electron spin density with oxygenation observed in evaporated a-Si.[29] (ii) In a-Si:H with low hydrogen content ($C_H = 7$ at. %) the relatively low PL efficiency is unaffected by light oxygenation ($C_O = 1.6$ at. %), although the FWHM, DOS, and $(\mu\tau)_p$ do show effects of additional gap states with oxygenation (see Table I). (iii) In more highly hydrogenated a-Si:H ($C_H = 14$ at. %) the oxygen ($C_O = 4.3$ and 5.7 at. %) leads to a reduction in the PL efficiency in addition to affecting the properties mentioned above. It appears that in highly hydrogenated films any defect compensation by oxygen, which is evident in unhydrogenated a-Si, is more than counterbalanced by an increase in the gap DOS with oxygen incorporation. These states may result from oxygen-induced or related defects in the a-Si:H network, or alternatively, oxygen may hinder more efficient elimination of the defects by hydrogen.

In Fig. 5, we present a schematic model showing the modifications in the gap DOS distribution based on the measurements described above. With oxygenation the gap is widened; the gap DOS near the valence band is increased and the valence-band

tail is broadened with respect to a-Si:H, as inferred from the absorption spectra extended by photoconductivity. The conduction-band tail width is also increased, as deduced from the increase of T_0; the midgap DOS is increased as deduced from capacitance-conductance measurements.

The mobility-lifetime products of holes $(\mu\tau)_p$ and electrons $(\mu\tau)_n$ follow an apparent reciprocal relation. To understand this, we consider the effect of the gap-state modifications just described on the trapping and recombination of the photocarriers. The increased gap-state density between midgap and the valence-band maximum can lead to a decrease in free-hole lifetime, either as a result of an increase in the density of recombination centers, or of a slow cascade of the holes through a succession of traps to the Fermi level without their reactivation to a conducting state, or of a bimolecular recombination process in the presence of hole trapping. The possibility of temporary trapping, whether followed by reactivation to a conducting hole state or by cascade to lower hole energies, can lead to an increased trapped-hole lifetime.

The increased gap-state density between midgap and the conduction-band edge can, in similar fashion, in principle lead to a decreased free-electron lifetime. However, the observed increase in $(\mu\tau)_n$ can be rationalized by the (reasonable) postulate that any possible decrease in τ_{free} produced by the states just below the conduction-band edge is more than offset by the increase in the trapped-hole lifetime: For this, one simply supposes that the photoelectrons may be reactivated into the conduction band as long as the holes are trapped in states with a low cross section for electron capture. The significant decrease in $(\mu\tau)_p$ (Table I) is of great consequence for the photovol-

taic conversion efficiency of a-Si:H based solar cells, which is limited mainly by the collection efficiency of holes.[30]

CONCLUSIONS

We find the following conclusions:

(1) The incorporation of oxygen into highly compensated a-Si:H leads to a broadening of the tails to both the conduction band and the valence band, an increase in the gap DOS, a decrease in the $(\mu\tau)_p$, and an increase in $(\mu\tau)_n$.

(2) Even a small atomic percentage of incorporated oxygen strongly reduces the hole $(\mu\tau)_p$, and hence is detrimental to solar-cell collection efficiency.

(3) The incorporation of oxygen into a-Si leads to significant PL, although the compensation of defects is not as efficient as with hydrogen.

(4) The oscillator strength of a Si-O vibrational mode at 1000 cm^{-1} is significantly smaller in the a-Si:H network than in the crystalline counterpart.

*Present address: Ecole Centrale de Lyon, ERA CNRS Génie Electronique (no. 661) 36 Route de Dardilly, 69130 Ecully, France.

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[19]Our calibration of hydrogen content to the integrated area of the Si-H wagging mode was deduced from a comparison of our results of hydrogen evolution, nuclear reaction, and infrared-absorption measurements on sputtered films. We define the hydrogen concentration C_H as $C_H(at. \%) = 100N_H/(N_H + N_{Si})$.

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