Optical dispersion relations in two types of amorphous silicon using Adachi's expression

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Using Adachi's expression [S. Adachi, Phys. Rev. B **43**, 12 316 (1991)] for the complex dielectric function of amorphous semiconductors, we fit out experimental results [M. Fried *et al.*, J. Appl. Phys. **71**, 5260 (1992)] for two different types (self-implanted and implanted-annealed or relaxed) of amorphous silicon. The complex dielectric functions were determined by spectroscopic ellipsometric measurements in the visible wavelength region. The fit resulted in different optical band gap (E_g) and damping (or broadening, Γ) energies. E_g is lower and Γ is higher in implanted *a*-Si. Both changes can be interpreted by the presence of more structural disorder point defects in implanted *a*-Si compared with relaxed *a*-Si.

INTRODUCTION

Understanding the structure and properties of *a*-Si is a scientific challenge of some complexity.¹ The problem is that there is not a single type of *a*-Si. There are several measurements which indicate that the properties of implanted amorphous silicon (*i*-*a*-Si) differ significantly from those of well relaxed (annealed) *a*-Si (*r*-*a*-Si).²⁻⁷

The best materials to use to investigate the properties of *a*-Si silicon are *i*-*a*-Si and *r*-*a*-Si made by self-implantation. There are no impurities and no voids in these samples which is not the case of samples made with other preparation methods, for example, sputtering or chemical-vapor deposition (CVD) -made *a*-Si. A small amount (below 1%) of incorporated hydrogen can significantly change the dielectric function of *a*-Si.⁸

It is of considerable interest to investigate the optical properties of amorphous semiconductors, especially amorphous silicon (*a*-Si). The most straightforward method is ellipsometry, because it can determine directly the complex refractive indices and the dielectric constants⁹ by measuring at even only one photon energy.

Earlier we determined the complex dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ of different kinds of amorphous silicon prepared by self-implantation and thermal relaxation (500 °C, 3 h).¹⁰ These measurements showed that the complex dielectric function (and thus the complex refractive index) of implanted *a*-Si (*i*-*a*-Si) differs from that of relaxed (annealed) *a*-Si (*r*-*a*-Si).

Very recently, Adachi published¹¹ a relatively simple model which claims to describe at the same time $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ in amorphous semiconductors. Adachi assumes that the imaginary part of the dielectric function (ϵ_2) yields a continuous absorption obeying the power law of $(\hbar\omega)^{-2}(\hbar\omega - E_g)^2$ and has a high-energy cutoff at E_c where E_g is the optical energy gap. Applying the Kramers-Kronig (KK) relation, Adachi obtained the expression for $\epsilon_1(\omega)$. By introducing a damping effect (i.e., broadening), the optical spectra became structureless

which is typically observed in amorphous semiconductors.

In this paper, we try to fit our experimental results¹⁰ with Adachi's expression and discuss the differences in the two different (implanted and relaxed) *a*-Si.

ADACHI'S MODEL (REF. 11)

The model is an extension of that of Tauc, Grigorovici, and Vancu.¹² The dielectric constant $\epsilon_2(\omega)$ for a crystal-line semiconductor is given by

$$\epsilon_2(\omega) = \left[\frac{2\pi e}{m\omega} \right]^2 \frac{2}{(2\pi)^3} \times \int_{BZ} d^3k |\mathbf{P}_{cv}(\mathbf{k})|^2 \delta[E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega], \quad (1)$$

where $\mathbf{P}_{cv}(\mathbf{k})$ is the momentum matrix element, *c* and *v* denote the conduction and valence bands, respectively, $E_c(\mathbf{k}) - E_v(\mathbf{k})$ is the interband energy, and the integration is performed over the first Brillouin zone.

It is well known that the valence and conduction bands retain their meaning even in the amorphous state. Assuming that the basic volume *V* contains the same number of atoms in the amorphous as in the crystalline state and that $\mathbf{P}_{cv}(\mathbf{k})$ is independent of *k* we obtain

$$\epsilon_2(\omega) = \left[\frac{2\pi e}{m\omega} \right]^2 \frac{(2\pi)^3}{2} \frac{1}{B_0} |\mathbf{P}_{cv}|^2 \times \int g_c(E^*) g_v(\hbar\omega - E^*) dE^*, \quad (2)$$

where g_c and g_v are the densities of states in the conduction and valence bands, respectively. It is apparent that $\epsilon_2(\omega)$ is determined by a convolution of the densities of states in the conduction and valence bands g_c and g_v for which energy is conserved. Substituting $g_c(E_n) \sim E_n^{1/2}$, $g_v(E_p) \sim E_p^{1/2}$ into Eq. (2) (where E_n , E_p , $E_n + E_p = \hbar\omega - E_g$ are measured from the band extrema, and E_g is the optical energy gap) we obtain

$$\varepsilon_2(\omega) = D(\hbar\omega)^{-2}(\hbar\omega - E_g)^2, \quad (3)$$

where D is a nondimensional strength parameter and E_g is the optical energy gap. If we plot $\hbar\omega\varepsilon_2(\omega)^{1/2}$ versus $\hbar\omega$ (Tauc plot¹²) near the band gap (i.e., below 3 eV) then we get the values of D and E_g from the linear extrapolation of the plot.

Adachi notes that expression (3) is almost identical to that of the indirect optical transitions in crystalline semiconductors,¹³

$$\varepsilon_2(\omega) = D(\hbar\omega)^{-2}(\hbar\omega - E_g)^2\Theta(1 - x_g) \quad (4)$$

with

$$x_g = E_g / \hbar\omega, \quad (5)$$

where $\Theta(z)$ is the Heaviside function given by

$$\Theta(z) = \begin{cases} 1 & \text{for } z \geq 0 \\ 0 & \text{for } z < 0 \end{cases} \quad (6)$$

The parabolic bands extending to infinite energies implied by Eq. (4) should be nonphysical. Modifying the model by taking into account a high-energy cutoff at en-

ergy E_c we can solve the Kramers-Kronig relation. The modification provides

$$\varepsilon_2(\omega) = D(\hbar\omega)^{-2}(\hbar\omega - E_g)^2\Theta(1 - x_g)\Theta(1 - x_c) \quad (7)$$

with

$$x_c = E_c / \hbar\omega. \quad (8)$$

The KK transformation of Eq. (7) gives

$$\varepsilon_1(\omega) = 1 + \frac{2D}{\pi} \left[-\frac{(E_g)^2}{(\hbar\omega)^2} \ln \left[\frac{E_c}{E_g} \right] + \frac{1}{2} \left[1 + \frac{E_g}{\hbar\omega} \right]^2 \ln \left[\frac{\hbar\omega + E_c}{\hbar\omega + E_g} \right] + \frac{1}{2} \left[1 - \frac{E_g}{\hbar\omega} \right]^2 \ln \left[\frac{\hbar\omega - E_c}{\hbar\omega - E_g} \right] \right]. \quad (9)$$

The $\varepsilon_1(\omega)$ spectrum of Eq. (9) exhibits a divergence at E_c . Adachi, therefore, introduces in this expression a damping effect in a phenomenological manner by replacing $\hbar\omega$ by $\hbar\omega + i\Gamma$. The contribution of optical transitions to $\varepsilon(\omega)$ in amorphous solids is finally written as

$$\varepsilon(\omega) = 1 + \frac{2D}{\pi} \left[-\frac{(E_g)^2}{(\hbar\omega + i\Gamma)^2} \ln \left[\frac{E_c}{E_g} \right] + \frac{1}{2} \left[1 + \frac{E_g}{\hbar\omega + i\Gamma} \right]^2 \ln \left[\frac{\hbar\omega + i\Gamma + E_c}{\hbar\omega + i\Gamma + E_g} \right] + \frac{1}{2} \left[1 - \frac{E_g}{\hbar\omega + i\Gamma} \right]^2 \ln \left[\frac{\hbar\omega + i\Gamma - E_c}{\hbar\omega + i\Gamma - E_g} \right] \right]. \quad (10)$$

The model described above requires four parameters, namely, E_g , E_c , D , and Γ . These parameters can be commonly used as adjustable constants for the calculations of both ε_1 and ε_2 , simultaneously.

RESULTS AND DISCUSSION

We have made the fit in three steps. First, we determined initial values of D and E_g from the Tauc plot¹² [Eq. (3)] between 2 and 3 eV. (This is the linear part of the curve.) Figure 1 shows the measured points and the fitted lines. Second, we made the fitting with these initial values, see Fig. 2, dashed lines. Third, we made a grid search around these values and we obtained better fits in both cases (*i-a-Si* and *r-a-Si*), see Fig. 2, solid lines. The obtained values are summarized in Table I.

The most apparent differences are the different band gap and damping energies. E_g is lower and Γ is higher in *i-a-Si*. Both changes can be interpreted by the presence of more structural disorder point defects in *i-a-Si*.

These point defects change the shape of the density of states (DOS) at the band edge compared with the continuous random-network (CRN) model.¹⁴ (This model based on a tetrahedrally coordinated random-network structure where each atom has four neighbors in an approximately tetrahedral arrangement; noncrystallinity is achieved through variations in the tetrahedral angle and through the relative rotation of adjoining tetrahedra.)

The point defects create new states in the band gap compared with a "perfect" CRN model decreasing E_g and increasing the absorption below 3 eV.

The change of Γ is analogous to the broadening of interband transitions in *c-Si* with temperature based on electron-phonon interaction.¹⁵ In that case a growth of

FIG. 1. Tauc (Ref. 12) plot of different types of amorphous silicon based on the relation $(\varepsilon_2 E^2)^{1/2} \approx (E - E_g)$, where E_g is the optical band-gap energy. The data are from Ref. 10.

FIG. 2. Complex dielectric functions of implanted, *i-a-Si* (a) and relaxed (implanted-annealed), *r-a-Si* (b), amorphous silicon and fitted curves by Adachi's expression. Dashed lines are the results of fitting with initial values from the Tauc plot (Fig. 1). Solid lines are the results of fitting using a grid search around these values. Parameters of curves are summarized in Table I. The data are from Ref. 10.

typically 0.1–0.2 eV in Γ (of different critical points) was measured from $T=0$ –900 K. In our case the point defects serve as scattering centers increasing Γ .

A similar effect was investigated in hydrogenated *a-Si*.^{16,17} Cody *et al.*¹⁶ found that the optical band gap is controlled by the amount of disorder, structural and thermal. Hydrogen affects the band gap only indirectly through its ability to relieve strain in the network. They compared the effects of structural and thermal disorder on the absorption edge by inducing structural disorder intentionally in the films by introducing dangling bonds through thermal evolution of hydrogen. Relatively simple model calculations¹⁶ gave the following expression for the optical band gap:

$$E_g(T, X) = E_g(0, 0) - P_d(\langle u^2 \rangle_X + \langle u^2 \rangle_T) \\ = E_g(0, 0) - P_d \langle u^2 \rangle_0 \left[X + \frac{2}{\exp(\theta/T) - 1} \right], \quad (11)$$

where $\langle u^2 \rangle_X$ is the contribution of structural (topological) disorder to the mean-square deviation of the atomic positions from a perfectly ordered configuration, $\langle u^2 \rangle_T$ is the averaged squared displacement of atoms due to thermal vibrations, $\langle u^2 \rangle_0$ is the zero-point uncertainty, $X = \langle u^2 \rangle_X / \langle u^2 \rangle_0$ is a measure of normalized disorder,

P_d is the deformation potential, and θ is a characteristic temperature of the phonon spectrum approximated by Einstein's one oscillator model. This expression separates the contribution of the static structural disorder and the dynamic phonon disorder. We think that a similar expression describes the change of the $\Gamma(T, X)$ broadening parameter.

We can express the change of E_g from Eq. (11) [$E_g(0, 0)$ and $\langle u^2 \rangle_T$ are eliminated]:

$$\Delta E_g = E_g(T, X_2) - E_g(T, X_1) = -P_d(\langle u^2 \rangle_{X_2} - \langle u^2 \rangle_{X_1}),$$

where X_2 and X_1 mean the disorder in the *i-a-Si* and *r-a-Si*, respectively.

Using the parameter value $P_d = 3000$ eV/nm² from Ref. 16 and $\Delta E_g = -0.21$ or $\Delta \Gamma = 0.24$ eV from the present work (see Table I), we get approximate values of $\Delta E_g / -P_d$ or $\Delta \Gamma / P_d = \Delta(\langle u^2 \rangle_X) = 7 \times 10^{-5}$ or 8×10^{-5} nm² (which means the difference of the averaged squared displacements of the atoms in the two types of *a-Si*). The averaged excess displacement is the square root of this value, i.e., 0.0084 or 0.0090 nm. (We consider the two values from ΔE_g and $\Delta \Gamma$ as error limits.) These values correspond to densities of displaced atoms of 1.5 or 1.7 at. %, relative to the 0.54-nm lattice parameter of silicon. These results are in surprisingly good agreement with the 2.2 ± 0.9 at. % and 1.6 at. % value determined

TABLE I. The results of fittings applying Eq. (10). $\sigma^2 = (\text{measured}^2 - \text{computed}^2) / (N - p)$, where N is the number of points and p is the number of parameters ($=4$).

E_g (eV)	E_c (eV)	D	Γ (eV)	σ^2	Line type in Fig. 2
<i>i-a-Si</i>					
1.24 ± 0.03	4.50 ± 0.05	86 ± 3	0.64 ± 0.06	6.2	dashed line
2.09 ± 0.02	4.00 ± 0.02	490 ± 3	1.09 ± 0.05	2.5	solid line
<i>r-a-Si</i>					
1.67 ± 0.04	4.67 ± 0.06	130 ± 5	0.49 ± 0.05	10.6	dashed line
2.30 ± 0.02	4.33 ± 0.03	484 ± 4	0.85 ± 0.05	6.0	solid line

by other methods such as impurity diffusion^{7,18} and photocarrier lifetime measurement.¹⁹

In Adachi's model, the strength parameter D is taken to be constant over energies of pair states between the conduction and valence bands. This assumption is usually made in the theory of optical properties of crystals. If we assume that D is a proper function of energy, the fit would be greatly improved. However, to check the valid-

ity of this energy dependence, we will require an exact electronic energy-band structure of the amorphous material, which is still an open question.

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