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CHARACTERIZING HYDROGENATED MICROCRYSTALLINE SILICON FILMS BY SPECTROSCOPIC ELLIPSOMETRY

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Characterizing Hydrogenated Microcrystalline Silicon Films by Spectroscopic Ellipsometry

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ABSTRACT

Effective medium models for microcrystalline silicon (μc-Si:H) films show only a limited ability to reproduce spectroscopic ellipsometry measurements of the film pseudodielectric function. It is proposed to determine first the dielectric function of the crystallite phase based on analysis of the third derivative of the spectral data, and then to use this in effective medium modeling instead of the crystalline silicon dielectric function.

I. INTRODUCTION

Hydrogenated microcrystalline silicon (μc-Si:H) is a promising material for thin film solar cells and thin film transistor arrays for flat panel displays. μc-Si:H produced by plasma-enhanced chemical vapor deposition (PECVD) consists in most cases of crystallites with dimensions ranging in the vicinity of 10-500 nm. These crystallites often exhibit a preferred orientation and are separated by regions of highly disordered material. The composition and structure of μc-Si:H depend strongly on preparation conditions. Analytic techniques commonly used to characterize μc-Si:H include X-ray analysis, TEM, AFM, FTIR, Raman spectroscopy, and spectroscopic ellipsometry (SE). Being a powerful nondestructive *in-situ* technique, SE plays an outstanding role in μc-Si:H diagnostics and analysis. SE spectra of a grown film contain information on its composition and structure. The common way to treat SE results is to convert the ellipsometric angles Ψ and Δ into the pseudodielectric function $\langle\varepsilon\rangle$:

$$\langle\varepsilon\rangle=\sin^2\Theta+((1-\rho)/(1+\rho))^2\cdot\sin^2\Theta\cdot\tan^2\Theta, \qquad (1)$$

where $\rho=\tan\Psi\cdot\exp(i\Delta)$, Θ is the angle of incidence. This formula supposes the sample to be semi-infinite with no overlayer on it. In many important cases one can adopt this assumption. Then $\langle\varepsilon\rangle$ is equal to the bulk dielectric function of the material studied.

μc-Si:H is a composite material and its dielectric function exhibits the critical point (CP) structure peculiar to crystalline Si superimposed on the broad spectrum of amorphous Si. The dielectric function of μc-Si:H is often derived from those of c-Si and a-Si using an appropriate effective medium approximation (EMA). Bruggeman EMA (BEMA) is believed to be the most appropriate for semiconductor materials. For a composite film of two phases it gives:

$$f_a\frac{\varepsilon_a-\langle\varepsilon\rangle}{\varepsilon_a+k\langle\varepsilon\rangle}+(1-f_a)\frac{\varepsilon_b-\langle\varepsilon\rangle}{\varepsilon_b+k\langle\varepsilon\rangle}=0, \qquad (2)$$

where ε_a and ε_b are the dielectric functions of the two components, and f_a is the fraction of one component. The screening factor k accounts for the accumulation of charge at the boundaries between separate phases. This factor incorporates the effect of the individual region shape that comprises the microstructure. If the composite film is macroscopically isotropic in two or three

dimensions then k=1 or 2, respectively. A BEMA model using a composite of c-Si, a-Si and voids shows only a limited ability to reproduce experimental SE data on μc-Si:H; this is because the optical properties of Si-based films are strongly affected by their microstructure. The authors of Ref.1 used a BEMA mixture of c-Si, a-Si and voids to model SE experimental data on μc-Si:H. The crystallite volume fraction X_c was thus estimated to range up to 48%, whereas other techniques (TEM and Raman spectroscopy) gave much higher values of X_c . Therefore the BEMA approach using c-Si, a-Si and voids seems to underestimate X_c . It was shown in Ref.2 that SE spectra of μc-Si:H could be better modeled by using the c-Si dielectric function with CP peaks artificially broadened by a fixed value of 50% or 100%. This led to an improved fit and 20% higher values for X_c . The authors of Ref.3 found that the dielectric function of the crystallite phase in μc-Si:H differs substantially from that of c-Si. The main difference was found to be the CP peak broadening, this being higher for μc-Si:H. An analogous conclusion was made in Ref.4. It was emphasized that the a-Si component in SE analysis may serve the additional role of simulating the broadening of optical transitions thereby making the SE interpretation ambiguous.

II. METHOD

It is proposed in this work to determine first the parameters of the dielectric function of the μc-Si:H film crystallite phase and then to use this in BEMA modeling instead of the c-Si dielectric function. An effective technique for determining these parameters is based on analysis of the second or third derivative of the experimental $\langle\varepsilon\rangle$ data with respect to photon energy [5,6]. This technique is very sensitive to crystallite phase CP parameters and is much less sensitive to a-Si, voids and different film overlayers. All these features can be introduced into an optical model of a μc-Si:H film via subsequent BEMA modeling.

The samples used in this work were μc-Si:H films deposited by PECVD on Corning 7059 glass.[7] The samples have different mean crystallite grain size $\langle L\rangle$ (110 - 230 Å) as determined by Scherrer's formula for the Si(111) X-ray diffraction peak. SE measurements were performed with a Jobin-Yvon UVISEL ellipsometer in the photon energy range of 1.5-5.0 eV at an angle of incidence of 70°.

Shown in Fig.1a,b are respectively the real and imaginary parts of the pseudodielectric function $\langle\varepsilon\rangle$ of films with different crystallite grain size. Since there are no interference fringes in the energy region of 2.2-5.0 eV the spectra presented characterize the films without any influence from the glass substrate. The spectra in Fig.1b reveal a smoothened double peak structure with maxima at about 3.4 eV (corresponding to the $E_0'+E_1$ transition of Si) and 4.3 eV (the $E_2(X)+E_2(\Sigma)$ transition of Si). This structure is typical for μc-Si:H.[6] BEMA modeling with library files for c-Si, a-Si, and voids does not give any reasonable fit for these films. To determine the $E_0'+E_1$ CP parameters we performed a line shape analysis of the third derivative of $\langle\varepsilon\rangle$.[5,8] Calculations show that the best fit is obtained with a two-dimensional CP. Functions of the form:

$$-2A \exp(i\varphi)\,(\omega - E + i\Gamma)^{-3} \qquad (3)$$

are fitted to $\langle\varepsilon\rangle'''$ in the vicinity of the $E_0'+E_1$ CP (about 3.4 eV), where ω is the photon energy. The CP is described by the amplitude A, threshold energy E, and broadening Γ, while φ represents the influence of adjacent CPs. Fitting the numerically calculated $\langle\varepsilon\rangle'''$ with the analytic function form (3) introduces systematic distortion to the values found for the CP parameters. To avoid this distortion we applied the technique of parallel numerical differentiation of the experimental SE data and of the theoretical model function for $\langle\varepsilon\rangle$.[8]

III. RESULTS AND DISCUSSION

The imaginary part of the third derivative of $\langle\varepsilon\rangle$ along with the best fit by line shape (3) is shown in Fig.2. The real part shows an analogous behavior. $\langle\varepsilon\rangle'''$ is well fitted by line shape (3) with Γ=0.168-0.197 eV. Broadening in this range as well as other CP parameters (Table 1) are typical for μc-Si:H.[6] Among these parameters E and Γ characterize the crystallite phase of μc-Si:H whereas A and φ can be substantially influenced by a-Si, voids and film

overlayer. This has been confirmed by applying the same calculation technique to the μc-Si:H model dielectric function prepared as stated below. The dependence of Γ on mean crystallite grain size <L> can be described by a linear relation [6]:

$$\Gamma = \Gamma_0 + \Gamma_{size} = \Gamma_0 + Q\langle L\rangle^{-1}, \quad (4)$$

where Γ_0 presents the intrinsic broadening of the bulk c-Si and a broadening due to disorder and impurities scattering. The Γ_{size} term explains the finite-size effect contribution. The experimental Γ vs $\langle L\rangle^{-1}$ dependence is shown in Fig.3. It is close to linear with Γ_0=0.144 eV and Q=6.154 eV·Å. This suggests that the $E_0'+E_1$ CP broadening is subjected to finite-size effects. So this dependence can be used to derive the mean crystallite grain size of PECVD-deposited μc-Si:H films from their SE spectra. Note that the crystallites are not perfect since Γ includes a crystallite size-independent contribution ($\Gamma_0 > \Gamma_{c\text{-}Si}$).

The CP parameters thus obtained are then used to model the dielectric function of the μc-Si:H crystallite phase. The two-dimensional CP function[5]:

$$\varepsilon(\omega) = C - A\exp(i\varphi)\ln(\omega - E + i\Gamma), \quad (5)$$

where C is a complex constant, is applied to μc-Si:H film BEMA modelling using Jobin-Yvon ellipsometric software. The optical model used is a single film plus overlayer system. The film bulk is modelled by a BEMA mixture of dielectric function (5) with the CP parameters E and Γ fixed at the values given in Table 1, a-Si taken from the software library, and voids. An overlayer of similar composition with higher void percentage is added to simulate the surface roughness. The parameters to be fitted are the volume fractions of the film and overlayer components (+thickness for overlayer), along with A, φ, and C values in (5). Results of the calculations are summarized in Table 2. The correlation matrix for each fit does not contain any element exceeding 0.9. This means in particular that including the constant C into the fit does not prevent other parameters from being fitted correctly. Note that the calculated void percentage includes not only the real porosity but also the hydrogen incorporated into the a-Si:H matrix.[6]

Then the (crystalline Si) / (crystalline Si+amorphous Si) percentage is 78%, 72%, and 68% for these samples whereas Raman spectroscopy[9] gives 83%, 79%, and 71%, respectively. The two sets of values are rather close and reveal the same tendency. This independent check shows that the proposed technique of treating the SE data is adequate for μc-Si:H films in a practical range of composition and crystallite grain size.

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FIGURE CAPTIONS

FIG. 1. a) The real, and b) the imaginary parts of the pseudodielectric function $\langle \varepsilon \rangle$ of films with different crystallite grain size L.

FIG. 2. The imaginary part of the third derivative of $\langle \varepsilon \rangle$ along with the best fit by the line shape in Eq. (3), for each of the films with different crystallite grain size L.

FIG. 3. The dependence of the estimated broadening, Γ, on the inverse grain size, $\langle L \rangle^{-1}$ for the three microcrystalline films represented in Figs. 1 and 2.

TABLE CAPTIONS

Table 1 The Critical Point parameters: threshold energy E, broadening Γ, amplitude A, and phase φ, for the films with different crystallite grain size $\langle L \rangle$.

Table 2 Results of the effective medium parameter fitting, assuming an overlayer on the film bulk, with the dielectric function of the μc-Si:H crystallite phase represented by the Critical Point model.

TABLE 1

<L> (Å)	E (eV)	Γ (eV)	A	φ (°)
230	3.366	0.168	0.802	80.920
170	3.384	0.185	2.448	86.334
110	3.403	0.197	3.350	92.922

TABLE 2

Grain	Film bulk			Overlayer				CP parameters		χ^2
size (Å)	cryst.Si (%)	a-Si (%)	void (%)	thickness (Å)	cryst.Si (%)	a-Si (%)	void (%)	A	φ	
230	59	17	24	39	27	24	49	1.013	86.139	0.404
170	68	27	5	8	39	19	42	1.862	81.662	0.397
110	68	32	0	2	58	21	21	2.892	81.506	0.327

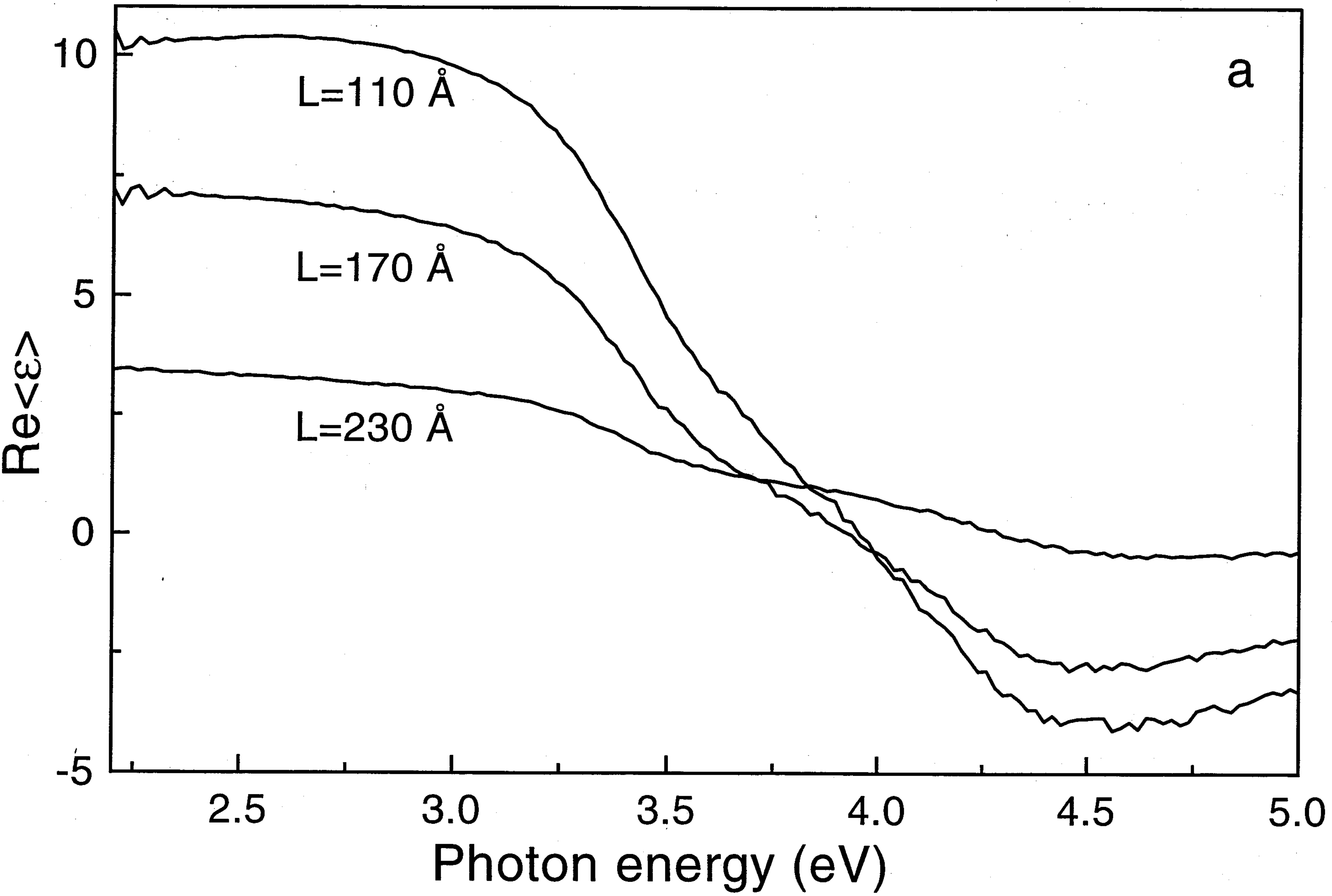

Fig. 1a)

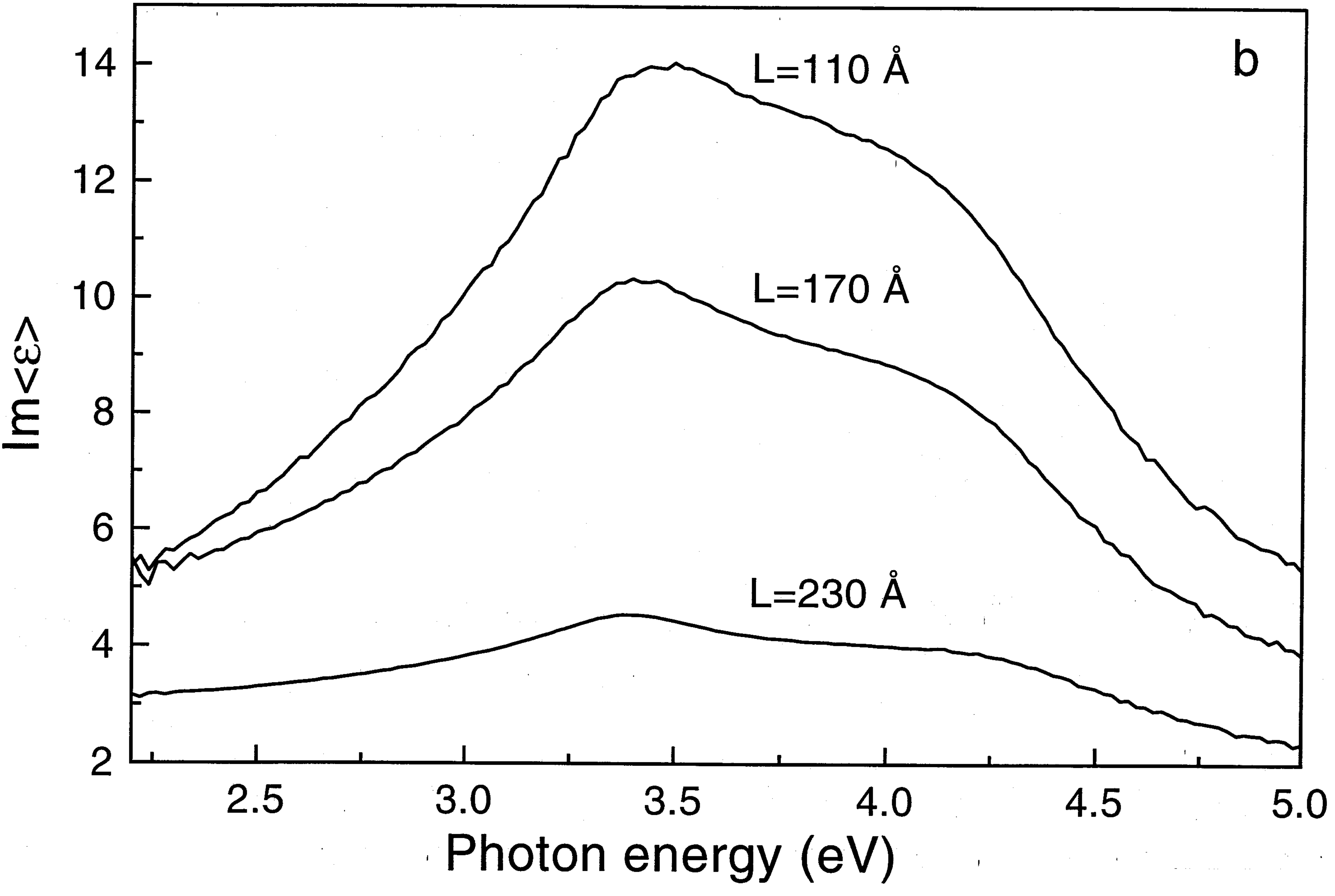

Fig. 1b)

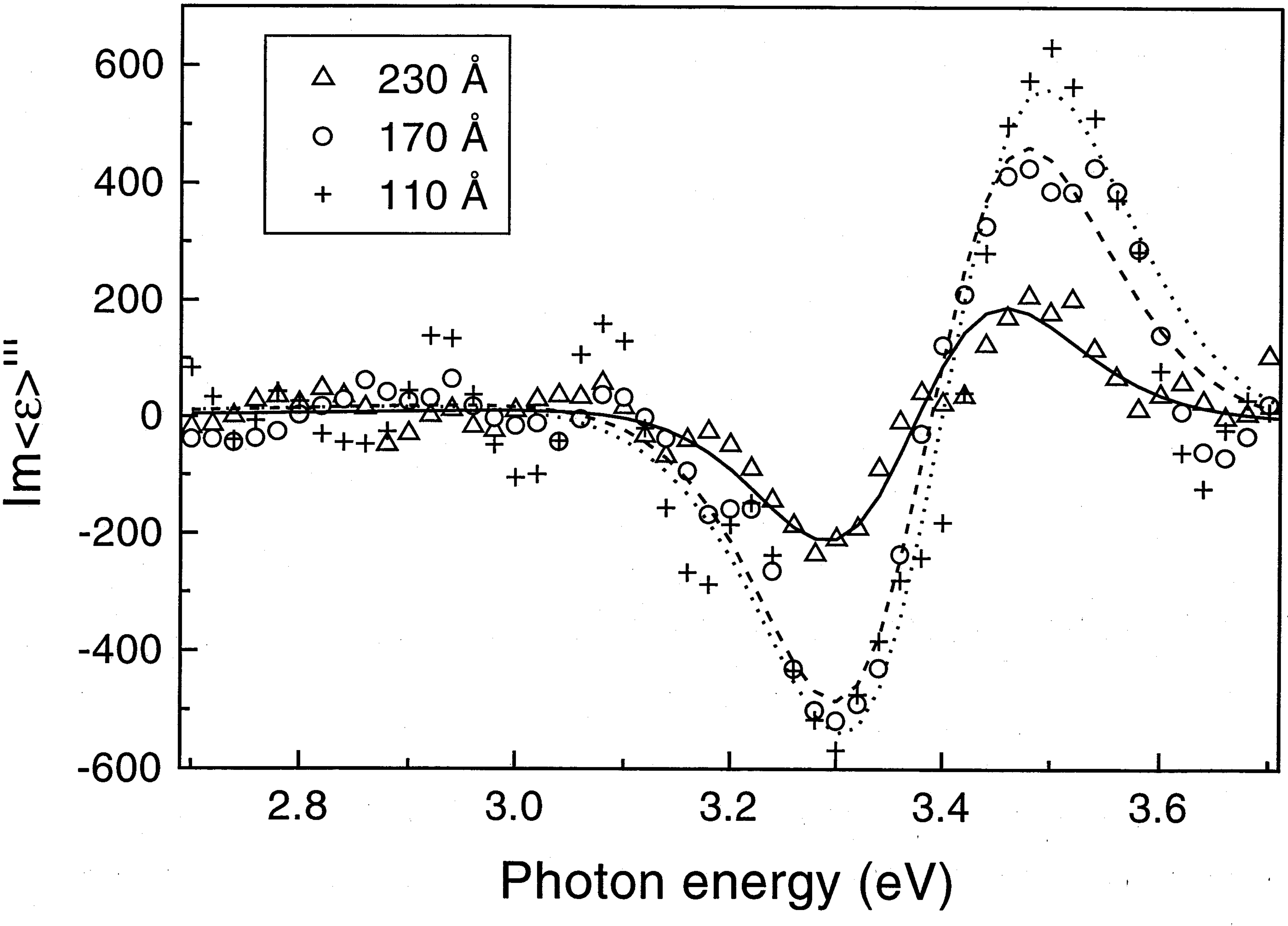

Fig. 2

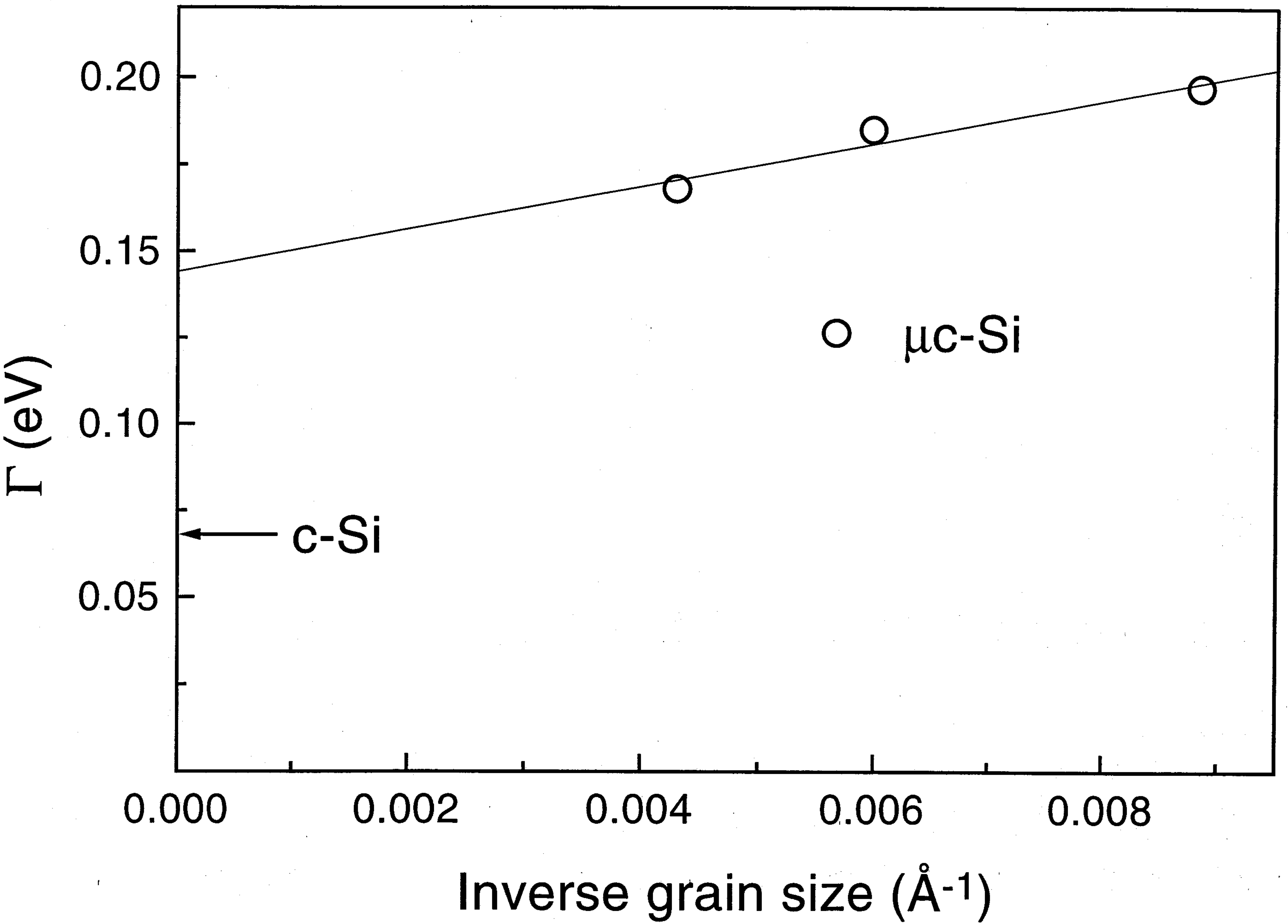

Fig. 3