Determination of optical constants of Si/ZnO polycrystalline nanocomposites by spectroscopic ellipsometry

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The optical constants of Si/ZnO composite films grown on quartz glass substrates were determined in the spectral range 1.5–5.0 eV by spectroscopic ellipsometry using a rotating-analyzer ellipsometer. The structure of the samples was modeled by a two-phase (substrate–film) model, and the optical functions of the film were parameterized through different effective medium approximations. The results allowed us to estimate the microstructural film parameters, such as film thickness, the volume fractions of each of the constituents, and optical constants.

I. INTRODUCTION

Nano- and microcomposites doped with semiconductor or metal have been extensively investigated in recent years due to their unique optical and dielectric properties, which favor their applications in electronics and gas sensors.[1] The study of the optical properties of composite films prepared on substrates requires the use of nondestructive characterization techniques that allow determination of the film parameters. One optical technique used for this purpose is spectroscopic ellipsometry, which is very sensitive to film thickness, surface roughness, optical constants, and other properties of interest. Spectroscopic ellipsometry measures the change in polarization of a linearly polarized, collimated beam after reflection from a sample surface.[2] The resulting state of polarization is characterized by the two so-called ellipsometric parameters, $\tan\Psi$ and $\cos\Delta$; the first one describes the ratio of the resulting amplitudes of two mutually perpendicular components of the reflected beam, whereas Δ represents the phase shift introduced by the reflection between these components. The ellipsometric parameters are related to the sample structure by

$$\tan\Psi \exp(i\Delta) = r_p / r_s = \rho \quad (1)$$

where r_p and r_s are the complex reflection coefficients[2] for the electric field of the incoming light polarized parallel and perpendicular to the plane of incidence, respectively. In the case in which the system is ambient-film-substrate (Fig. 1), these reflection coefficients are described by the equations:

$$r_p = \frac{(r_{01})_P + (r_{12})_P e^{-2i\beta}}{1 + (r_{01})_P (r_{12})_P e^{-2i\beta}} \quad , \quad (2)$$

$$r_s = \frac{(r_{01})_S + (r_{12})_S e^{-2i\beta}}{1 + (r_{01})_S (r_{12})_S e^{-2i\beta}} \quad , \quad (3)$$

where β is the phase change that the multiply reflected wave inside the film experiences as it traverses the film once from one boundary to the other and is given in terms of the free-space wavelength λ, the film thickness d_1, the

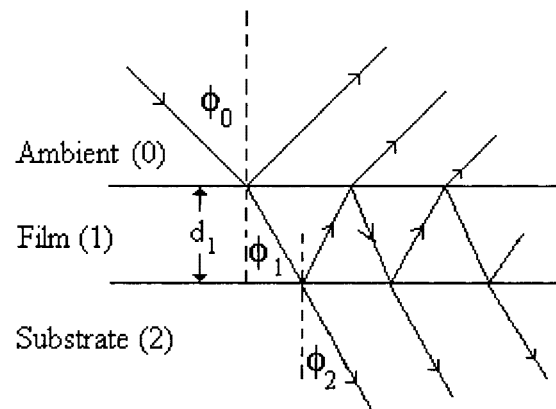

FIG. 1. Schematic diagram of the reflection at different interfaces of an ambient-film-substrate system.

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film complex index of refraction N_1 and the (complex) angle of refraction in the film ϕ_1 (the angle between the direction of propagation of the zig-zag wave in the film and the normal to the film boundaries) as

$$\beta = \frac{2\pi d_1}{\lambda} N_1 \cos\phi_1 \quad . \tag{4}$$

For the system ambient-film-substrate, ρ determines the complex pseudo-dielectric function:

$$\langle\epsilon\rangle = \langle\epsilon_1\rangle + i\langle\epsilon_2\rangle = \sin^2\phi_0 \{1 + \tan^2\phi_0 [(1 - \rho)/(1 + \rho)]^2\} \quad . \tag{5}$$

Other optical constants, such as refractive index n and absorption index k are derived from $\langle\epsilon\rangle$ since $\langle n\rangle + i\langle k\rangle = \langle\epsilon\rangle^{1/2}$ or equivalently $\langle\epsilon_1\rangle = \langle n\rangle^2 - \langle k\rangle^2$ and $\langle\epsilon_2\rangle = 2\langle n\rangle\langle k\rangle$. Model parameters, such as film thickness and composition, are varied to obtain a best X^2 fit to the measured parameters $\tan\Psi$ and $\cos\Delta$ as described by Jellison.[3]

In this study, we describe the results of spectroscopic ellipsometry measurements on several samples of Si/ZnO composite films prepared on quartz glass substrate and annealed at different temperatures. The measurements were done in the spectral range 1.5–5.0 eV with a rotating-analyzer ellipsometer. The film thickness, volume fractions of each of the constituents of the films, complex dielectric function, and other quantities, such as the refractive index and absorption index, were estimated for the Si/ZnO composites.

II. EXPERIMENTAL

Si/ZnO composite films were prepared on quartz glass (Nihon Rika Garasu Kogyo, Japan) substrates by co-sputtering technique with a radio-frequency (rf) sputtering apparatus (Shimadzu HSR-521). Eight Si wafers of $5 \times 5 \times 0.3$ mm size were placed symmetrically on a 100 mm diameter ZnO target and sputtered with 100 W rf power at 10 mtorr Ar gas pressure. Some samples were annealed at 400, 600, and 800 °C for 5 h in vacuum (2×10^{-6} torr). The Si/ZnO films used for the transmission electron microscopy (TEM) study, were deposited on carbon-covered Cu grids. A JEOL JEM2000-FXII electron microscope was used for the TEM observations. The chemical composition of the films and the chemical state of the individual elements were studied by a Perkin-Elmer (PHI 5600ci) x-ray photoelectron spectroscopy (XPS) system. The optical measurements of the composite samples were performed with a rotating-analyzer ellipsometer. As the light source, a xenon-mercury lamp the 75 W was used. The light from the source was allowed to passed through a Cary monochromator (with 10 Å spectral resolution at 2341 Å) to have a monochromatic beam. The light beam with a definite wavelength fell on a polarizer prism (Rochon prism), which produced a linearly polarized light beam. The polarized beam is then incided on the samples surface at various angles of incidence. The reflected beam was passed through the other polarizator (analyzer) rotating about its optical axis with a frequency of 3600 rpm. The intensity of the reflected beam was measured with a photomultiplier tube and analyzed through a Stanford Research (model SR760) spectrum analyzer. The measurements and analysis of the samples were carried out in the spectral range 1.5 to 5.0 eV. Measurements carried out at different spots on the sample showed no variation in the ellipsometric data.

III. RESULTS AND DISCUSSION

A. Microstructural characterization

The microstructure of the Si/ZnO composites was studied by TEM. Figure 2 shows the typical micrographs for the as-grown and 800 °C annealed films. The films are seen to consist of fine partially oxidized Si particles homogeneously dispersed in the matrix. We found that the as-deposited films consist of nanoparticles of size ranging from 2 to 4 nm. In the films annealed at 400 and 600°C, the dimension of the nanoparticles did not increase noticeably. When the annealing temperature of the samples increased to 800 °C, a considerable increment in the dimension of the particles was observed. Figure 3 shows the variation of the average particles size with annealing temperature, obtained from the electron micrographs by measurement of the linear dimensions of approximately 30% of the total number of particles. The average particle size depended on the annealing temperature of the samples. It is evident that at annealing temperatures near 800 °C the small nanoparticles aggregate to form bigger particles (microclusters hereafter). In the films annealed at 800 °C, the average size of the microclusters was 46 nm.

B. Compositional characterization

In Fig. 4, we show the evolution of the Si_{2p} emission peak with the variation of the annealing temperature of the composite films. The peak positions varied progressively as annealing temperature increased, but remained in between the peak positions of Si in elemental Si (99.2 eV) and SiO_2 (103.9 eV). This suggests that Si incorporated in the films, remain in the SiO_x ($0 < x < 2$) chemical state. Several authors[4–6] proposed that a shift of the Si_{2p} peak should be attributed to the charge transfer from Si to more electronegative O atoms. For the SiO_x alloys from $x = 0$ to 2 deposited by reactive sputtering, Bell and Ley[4] observed that the binding energy of the Si_{2p} peak shifts continuously over the entire concentration range, and they interpreted this phenomenon in

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terms of a chemical shift of the Si_{2p} core level due to charge transfer from Si to O. In the Fig. 4, the Si_{2p} peak shifted progressively to higher binding energy when the annealing temperature of the films increased. This effect indicates that as the annealing temperature increases, the charge transfer from Si to O is favored.

To estimate the degree of oxidation of silicon in the Si/ZnO composite films, we used the values of binding energy of the Si_{2p} peak for the SiO_x alloys reported by Bell and Ley[4] (see Fig. 5). We could evaluate that $x = 0.60$ corresponds to the as deposited films and $x = 0.64$, 0.70 and 1.10 to the films annealed at 400, 600, and 800 °C, respectively.

C. Optical characterization

For the analysis of the experimental ellipsometric spectra of the Si/ZnO composite samples annealed at different temperatures, we considered several models for

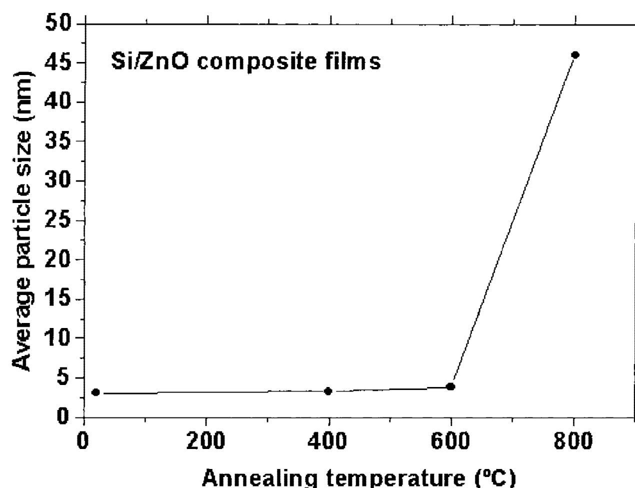
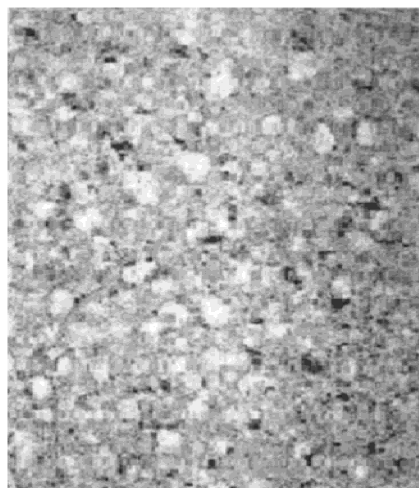


FIG. 3. Dependence of average particle size on annealed temperature for Si/ZnO composite films.



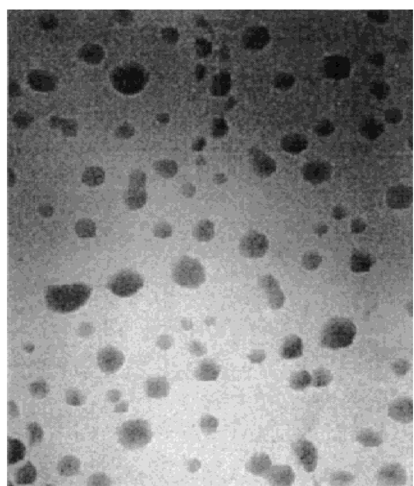


FIG. 2. TEM images of Si/ZnO composite films (a) as deposited and (b) annealed at 800 °C.

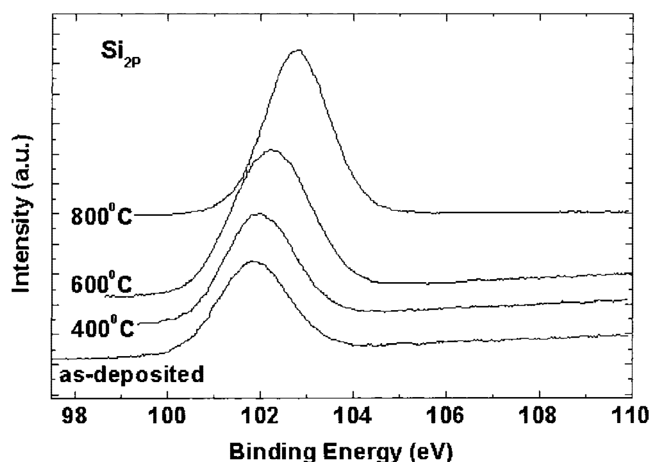


FIG. 4. Evolution of the XPS Si_{2p} emission peak with the variation of the annealing temperature.

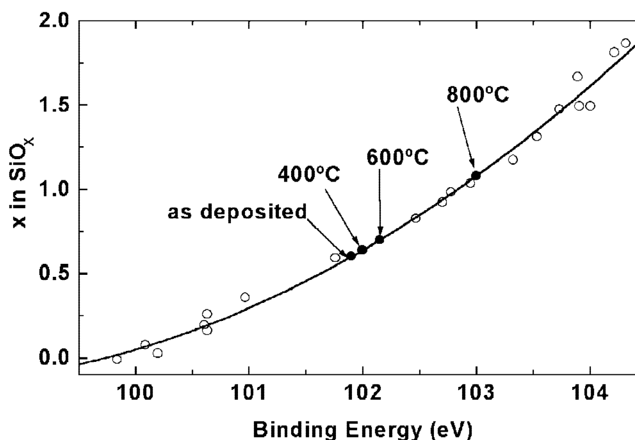


FIG. 5. Si_{2p} peak position of the XPS spectra as the function of oxygen concentration. Open circles are XPS results of SiO_x ($0 \leq x \leq 2$) alloys given by Bell and Ley,[4] solid circles are results of Si/ZnO composite films annealed at different temperatures.

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the optical response of the samples, but only the model that gave the best fit to the experimental data is presented in this work. In the model proposed, the sample was assumed to consist of a composite layer on a substrate of SiO_2. The layer consisting of a physical mixture of ZnO, SiO_x and voids, was modeled through the well-known Bruggeman[7] effective medium expression

$$f_{\mathrm{ZnO}} \frac{\epsilon_{\mathrm{ZnO}} - \langle\epsilon\rangle}{\epsilon_{\mathrm{ZnO}} + 2\langle\epsilon\rangle} + f_{\mathrm{SiO_x}} \frac{\epsilon_{\mathrm{SiO}_x} - \langle\epsilon\rangle}{\epsilon_{\mathrm{SiO}_x} + 2\langle\epsilon\rangle} + f_{\mathrm{voids}} \frac{\epsilon_{\mathrm{voids}} - \langle\epsilon\rangle}{\epsilon_{\mathrm{voids}} + 2\langle\epsilon\rangle} = 0 \quad , \qquad (6)$$

where $\langle\epsilon\rangle$ is the effective dielectric function of the composite mixture, ϵ_{ZnO}, $\epsilon_{\mathrm{SiO}_x}$, $\epsilon_{\mathrm{voids}}$ and $f_{\mathrm{ZnO}}, f_{\mathrm{SiO}_x}, f_{\mathrm{voids}}$ are the dielectric functions and volume fractions of ZnO, SiO_x, and vacuum, respectively.

The fitting to the experimental data was carried out by parametrization of the optical functions for ZnO through the procedure of Forouhi and Bloomer (FB),[8] which is often used to approximate the optical functions of amorphous semiconductor materials. Such expression is given in terms of the components of the complex index of refraction:

$$n(E) = n_{\mathrm{X}} + \frac{\mathrm{B}_0 E + \mathrm{C}_0}{E^2 - BE + \mathrm{C}} \quad , \qquad (7)$$

$$k(E) = \frac{\mathrm{A}(E - E_g)^2}{E^2 - \mathrm{B}E + \mathrm{C}} \quad , \qquad (8)$$

where

$$\mathrm{B}_0 = \frac{\mathrm{A}}{Q}\left[-\frac{\mathrm{B}^2}{2} + E_g\mathrm{B} - E_g^2 + \mathrm{C}\right] \quad , \qquad (9)$$

$$\mathrm{C}_0 = \frac{\mathrm{A}}{Q}\left[(E_g^2 + \mathrm{C})\,\frac{\mathrm{B}}{2} - 2E_g\mathrm{C}\right] \quad , \qquad (10)$$

$$Q = ½\,(4\mathrm{C} - \mathrm{B}^2)^{1/2} \quad . \qquad (11)$$

In the relations for $n(E)$ and $k(E)$, $n(\infty)$ is the value of n when $E \rightarrow \infty$ and is greater than unity, E_g represents the optical energy band gap. A, B, and C are positive nonzero constants characteristic of the medium such that $4C - B^2 > 0$. Finally, B_0 and C_0 are constants that depend on A, B, C, and E_g.

The optical response of the SiO_x component was simulated though the Lorentz Oscillator Approximation (LOA),[9] which is frequently used for materials constituting of a mixture of crystalline and amorphous phases. In the LOA approximation, the expression of the dielectric function is given by

$$\epsilon = \epsilon_x + \frac{(\epsilon_s - \epsilon_x)E_{\mathrm{T}}^2}{E_{\mathrm{T}}^2 - E^2 + i\Gamma_0 E} \quad , \qquad (12)$$

where ϵ_∞ is the dielectric function when $E \rightarrow \infty$ (higher frequencies limit), ϵ_s is the static dielectric function (lower frequencies limit), E_T is the energy of the harmonic oscillator and Γ_0 is a broadening parameter.

Our model allowed us to fit the optical functions of the Si/ZnO composite films with the parameters given by FB and LOA approximations, in addition to their structural parameters like volume fractions of each of the constituents (ZnO, SiO_x and void) and the thickness of the films, using Eq. (6).

Figure 6 shows the variations of the measured pseudo-ellipsometric parameters $\langle\tan\Psi\rangle$ and $\langle\cos\Delta\rangle$ in the spectral range 1.5–5.0 eV for the as-deposited (a) and 800 °C annealed (b) Si/ZnO films, at a 60° angle of incidence. The dashed curves represent the fittings obtained through our model. The fits show a good agreement with the experimental data even in the part of the spectrum where the optical interference effects of the layer become apparent (in the region <3.5 eV), shown by the peaks and valleys in the experimental spectrum. Such interference effect is not dependent on the angle of incidence since measurements of the composite samples at different

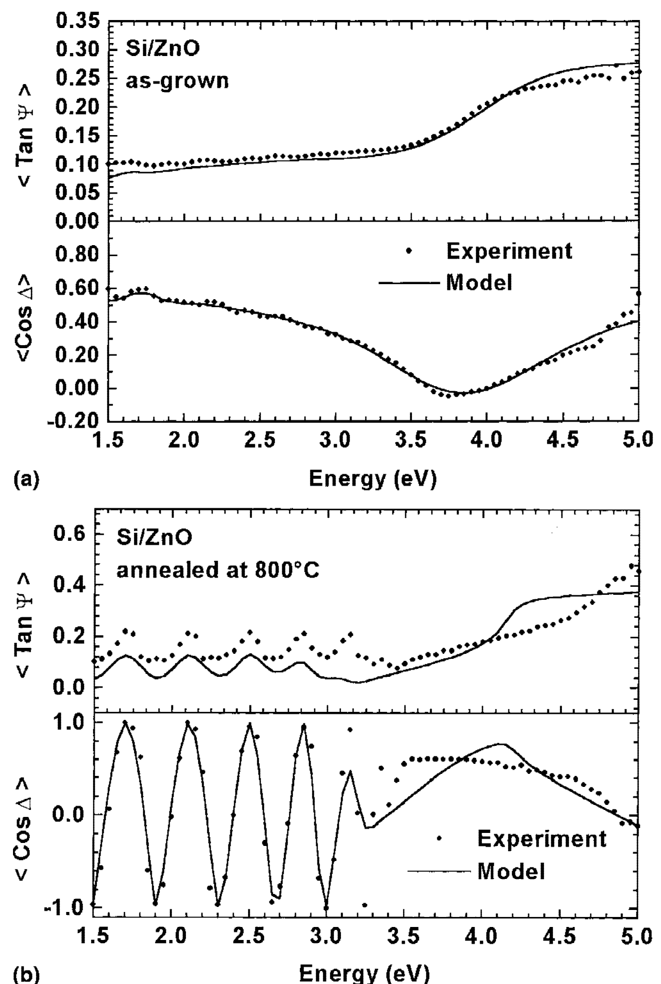

FIG. 6. Best fit curves for tan Ψ and cos Δ for Si/ZnO samples (a) as grown and (b) 800 °C annealed.

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angles of incidence (55°, 60°, and 65°) also revealed this oscillatory behavior. In the spectra of as-deposited samples, the light did not penetrate appreciably into the composite layer, which is evident from the small oscillations, indicating that the optical response is representative only of the sample surface, including the surface over layers such as roughness or surface oxide. Nevertheless, in the composite samples annealed at 800 °C, the interference effects of the layer are clearly seen for $E <$ 3.5 eV. The structural parameters obtained by fitting of the experimental data indicate that the analyzed samples consist of a film of approximately 1 μm thick on a SiO_2 substrate. The films consist of ZnO, void, and partially oxidized silicon (SiO_x). The volume fraction of SiO_x did not vary considerably with the variation of annealing temperature. The parameters of the fit are given in Table I.

The pseudo-dielectric functions $\langle \epsilon \rangle$ of the Si/ZnO composite films, as-grown and annealed at 400, 600 and 800 °C were determined by the results of the fits and resolving the ellipsometric equations for $\langle \epsilon \rangle$ of the films. The calculated $\langle \epsilon \rangle$ for the Si/ZnO composite films, and the dielectric function of crystalline ZnO taken from the work of Freeouf[10] are shown in the Fig. 7. We observed that the dielectric response ($\langle \epsilon_1 \rangle$ and $\langle \epsilon_2 \rangle$) of the as-deposited films presents a broad band above 3.5 eV, characteristic of an amorphous phase of the ZnO matrix. These results agree with the XRD analysis of the Si/ZnO composite films reported by Pal *et al.*[11] On incorporation of Si in the matrix, the band became more intense and shifted toward higher energy. The increase of intensity of the band and its broadness might be due to the increase of amorphous phase of the martix on incorporation of Si in the films. The reason for the shift of the band toward higher energy is not very clear for the moment, but it might have some relation to the incorporation of partially oxidized silicon nanoparticles in the samples.

TABLE I. Values of different parameters obtained from ellipsometric results and their theoretical fittings.

Parameter	As deposited	Annealed at 800 °C
No. of films	1	1
Thickness	10468 Å ± 290.818	10406 Å ± 68.123
f_{ZnO}	31.27 ± 2.323	46.38 ± 9.032
f_{SiO_x}	16.63 ± 1.133	18.36 ± 5.483
f_{air}	52.11	35.26
n_∞	1.755 ± 0.158	2.513 ± 0.678
A	0.263 ± 0.035	0.183 ± 0.089
B	7.994 ± 0.073	6.893 ± 0.267
C	16.348 ± 0.298	12.251 ± 0.888
E_g	2.893 ± 0.103	2.553 ± 0.171
ϵ_∞	0.131 ± 0.091	2.093 ± 0.694
ϵ_s	17.783 ± 1.441	0.733 ± 0.311
E_T	4.783 ± 0.330	5.609 ± 0.310
Γ_0	17.982 ± 1.785	0.130 ± 0.120

For the films annealed at higher temperatures, due to crystallization of the matrix, the contribution of the ZnO amorphous phase is lower (as indicated by the reduction of the broadness of the band). On increasing the annealing tempartature, the band became less intense and shifted toward lower energy. The shift of the band toward lower energy might be the result of the combined effects of the increase of crystallite size of the ZnO matrix and the increase of the size of the incorporated nanoparticles. When the annealing temperature was increased to 600 °C, the pseudo-dielectric functions revealed another band located at around 4.65 eV for $\langle \epsilon_1 \rangle$ and at around 4.8 eV for $\langle \epsilon_2 \rangle$. This higher energy band was assigned to the SiO_x present in the films. We find that the position of this band is shifted by about 1.20 eV with respect to that of SiO.[12] For the films annealed at 800 °C, we could not

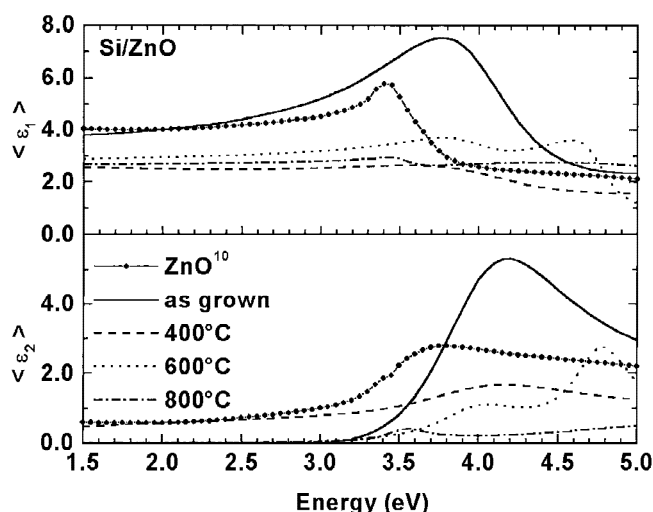

FIG. 7. Real and imaginary parts of the dielectric function of Si/ZnO composite films as derived from ellipsometry data.

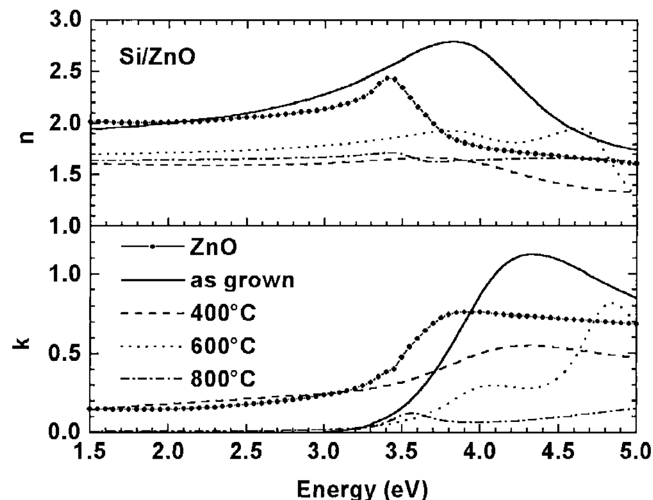

FIG. 8. Optical constants *n* and *k* for Si/ZnO composite films determined ellipsometrically.

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observe any band in between 4.0 and 5.0 eV. However, a close observation of the pseudo-dielectric function curves (Fig. 7) indicates that there might be another band at energy beyond 5.0 eV not revealed due to the wavelength limitation of our experiments. We think that the response of the SiO_x component might be revealed around 5.5 eV. Moreover, the XPS results indicate that the oxidized state of silicon increases when the annealing temperature of the films is increased.

The optical constants refractive index n and absorption index k were derived from these results and are presented in Fig. 8. A complex evolution of n and k has been obtained for the composite films depending on their temperature of annealing, which might be related to the microstructural change of both the matrix and the nanometric clusters embedded in it.

IV. CONCLUSION

The micro structural and optical parameters of the Si/ZnO composite films have been obtained for the first time. With the increase of annealing temperature, the crystallinity of the ZnO matrix and the oxidation state of Si clusters increased. The optical constants (n and k) of the composite films depends on the microstructure of the matrix and the nanoclusters embedded in it.

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