RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 36, NUMBER 11 15 OCTOBER 1987-I

Nonuniformity in void concentration between the initial and final growth stage of sputtered *a*-Ge films studied using spectroscopic ellipsometry

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(Received 8 June 1987)

In this study *a*-Ge films were sputtered onto 60° vitreous silica prisms. The films were examined by spectroscopic ellipsometry at the prism-film and air-film interfaces. The void fraction was found to be significantly different near these two interfaces for an rf-sputtered film but almost the same for a dc-magnetron-sputtered film. This difference between depositions is related to a higher degree of energetic particle bombardment in the latter case. Previous studies of the thickness dependence of void fraction in the film were done on different films of various thickness, while the present measurements were performed on the same film and thus directly verify the nonuniformity in the void concentration in rf-sputtered films.

There is an increasing interest in the variation of thin-film morphology with film thickness and its relationship with measured physical properties. Changes in resistivity, optical constants, and dielectric breakdown with film thickness have been reported.[1-3] These reports typically identify the film inhomogeneity as an underlying cause for the changes with thickness. Spectroscopic ellipsometry (SE) is an excellent means of studying the density of thin films by utilizing a light beam from the near-uv to the near-ir region as the nondestructive probe.

Previous SE studies[4,5] have shown that the optical properties vary with film thickness and thus can be explained as due to changes in the void fraction. The gradient in the void fraction was measured on a series of *a*-Ge films of different thicknesses where the probe depth is estimated to be a few hundred angstroms below the surface of the film in the spectral region of interest. Optical band-gap measurements on these films indicate that the void fraction influences the calculated band gap.[5] In this report we show that by depositing *a*-Ge films on a 60° prism the initial and final 500–1000-Å growth of a sputtered film can be investigated.

Amorphous Ge films were deposited onto 60° vitreous silica prisms by rf-diode- and dc-magnetron-sputtering techniques. The rf-sputtering unit was a MRC model 8500 with an argon-gas pressure of 20 mTorr, power of 100 W, and target-to-substrate distance of 27 mm. The dc-magnetron-sputtering source was an US Gun II model 500 operated at an argon-gas pressure of 1 mTorr, power of 100 W, target voltage 430 V, and target-to-substrate distance of 100 mm. In both systems the temperature rise during the deposition for the approximately 1600-Å-thick films was 40 °C.

A schematic of the experimental arrangement for the optical measurements is shown in Fig. 1. The incident beam was oriented strictly perpendicular to the prism surface in order to avoid introducing any additional change of polarization state due to non-normal incidence at the prism-ambient boundary. This was accomplished by adjusting the prism orientation in such a way that the reflected beam from the air-prism surface coincides with the incident beam. The exit beam would also be normal to the second prism surface only if prism angles β and γ are equal (see Fig. 1). The prism angles were accurately measured by a Gaertner precision research spectrometer, and the difference between β and γ was found to be 0.2°. This means the exit beam deviates from normal by an amount $\delta=\beta-\gamma$. The additional polarization change caused by this angle variation was calculated by using Fresnel's formula, and the correction was found to be negligibly small. In fact, for small δ the correction to the ellipsometric parameters is proportional to δ^2, which is of the order of 10^{-5} in this case.

The complex pseudodielectric function was evaluated from the ellipsometric data ρ and the angle of incidence ϕ with the relation

$$\epsilon/\epsilon_0=\sin^2\phi+(1-\rho)^2(1+\rho)^{-2}\sin^2\phi\tan^2\phi ,$$

where $\rho=\tan\Psi\exp(i\Delta)$, ϵ is the pseudodielectric function of the film, ϵ_0 is the dielectric function of the ambient surroundings, and Δ and Ψ are the measured ellipsometric parameters at the wavelength λ. The values of ϵ_0 used in the calculations for the air-film interface and film-prism interface are those of air and vitreous silica, respectively.

Figures 2 and 3 show the imaginary part of the pseudo-

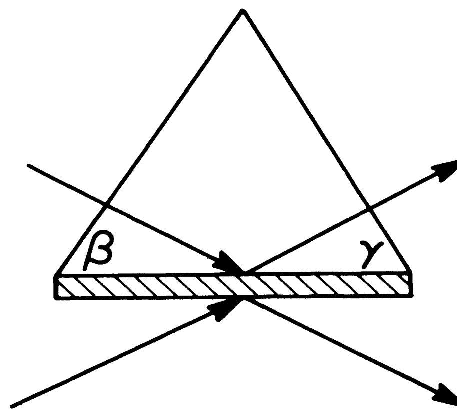

FIG. 1. Schematic of the ellipsometric measurements on the air-film and prism-film sides of an *a*-Ge film.

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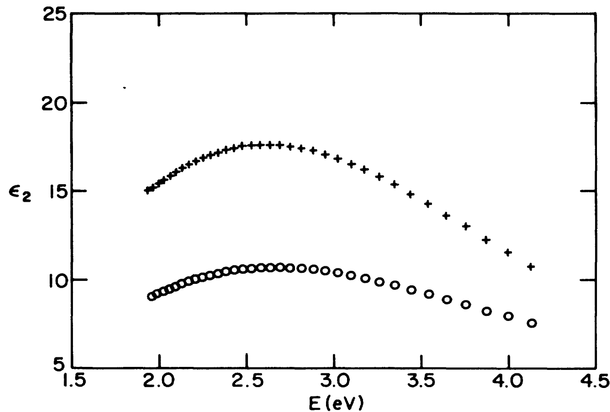

FIG. 2. Imaginary part of the pseudodielectric functions for rf-sputtered film: from air-film interface (+++) and from prism-film interface (ooo).

dielectric function (ϵ_2) as calculated from the SE measurements on both sides of the films. The difference in the spectra for the rf-sputtered film can be easily seen; however, for the dc-magnetron film, the difference is very small. The reduction in peak height for the rf film is directly attributed to the difference in void fraction between the two sides of the same film.

The modeling procedure used here to determine the void fraction is described elsewhere.[6] The Bruggeman effective-medium theory[7] was used in the calculation using the reference data on dielectric functions for *a*-Ge and GeO_2 taken from the literature.[8,9] The side of the film exposed to air was modeled as a substrate-overlayer system with the substrate treated as a mixture of *a*-Ge and voids, and the overlayer was taken to be GeO_2. On the other hand, the prism side of the film was modeled without an overlayer for the rf-sputtered film and with a microscopically rough surface layer for the dc-magnetron film. This does not imply the lack of surface roughness in the rf-sputter-deposited film. On the contrary, the rf film is so filled with voids throughout the probing region that one cannot use an abrupt microscopically rough surface-layer model. The difference in the void fraction between the top and bottom layers in the rf film is about 24% with the air-

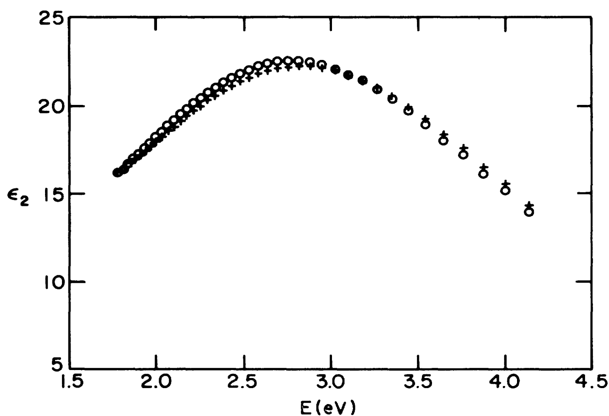

FIG. 3. Imaginary part of the pseudodielectric functions for dc-magnetron-sputtered film: from air-film interface (+++) and from prism-film interface (ooo).

film surface region being denser. The dc magnetron film is slightly denser than the reference sample (3% lower than crystalline Ge, as described in the previous study[8]), with the prism-film surface region being 3% denser and the air-film surface region having the same value as the reference. We should also mention that the air-film side is not free of microscopic roughness, as pointed out by Blanco, McMarr, and Vedam;[10] however, they found the model using microscopic roughness as an overlayer did not affect the void-fraction value beneath the top surface significantly. Since GeO_2 is soluble in water, McMarr, Blanco, and Vedam[11] washed the GeO_2 overlayer with water and found that the thickness of the overlayer was reduced but the void fraction of Ge was almost unchanged.

The low-density network usually manifests itself as a correlated density variation in an overfocused or underfocused phase-contrast transmission electron microscopy (TEM) image. In Fig. 4 the difference in the void network between the rf diode and dc-magnetron samples is

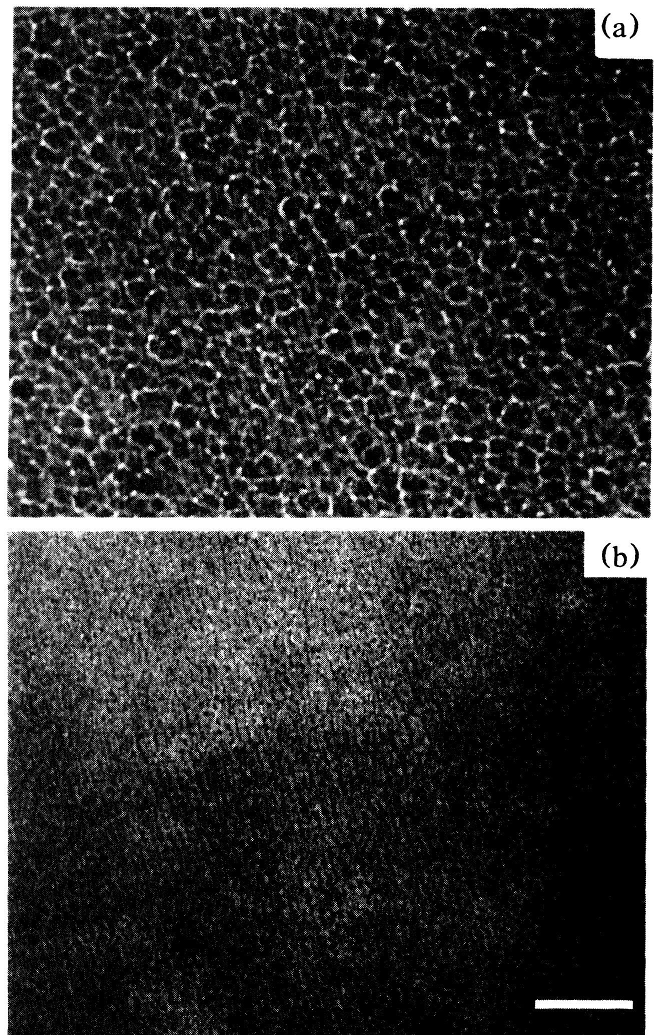

FIG. 4. TEM micrographs of ~500-Å-thick *a*-Ge films. (a) rf sputtered at 20-mTorr Ar pressure; (b) dc-magnetron sputtered at 1-mTorr Ar pressure. The bar marker represents 500 Å.

quite apparent by the absence of any observable network structure in the TEM micrograph of the latter. It is important to note, however, that this evidence should not be interpreted to mean that there are no voids in the dc-magnetron films. As shown previously *a*-Ge can even have a density as high as 5% greater than crystalline Ge density, depending on the preparation conditions.[12]

The present experiments determine the void fraction in the films on both sides of the same film and clearly establish that the void network in the rf-sputtered film is not uniform but actually varies with thickness. It should be mentioned that this phenomenon is not limited to *a*-Ge films. In general, films deposited under low-mobility conditions typically show inhomogeneity in their structural morphology and their resulting properties as a function of preparation conditions. For the present films, the difference in structural morphology possibly arises from a difference in the ion bombardment of the film during growth, since the other two primary mobility processes, film temperature and chemistry, are essentially the same. In rf sputtering at pressures ≥ 20 mTorr the substrate negative self-bias potentials are generally less than 10 V, and the higher-energy sputtered species are moderated through gas-phase collisions.[13] Although the substrate self-bias potential is usually even lower for magnetron sputtering, the lower gas pressure (1 mTorr) allows the sputtered species to arrive at the growing film with approximately their initial energies, where the higher-energy component (≥ 50 eV) is not negligible.[14] Also, for the same reason, elastically backscattered species from the target will be more energetic in the case of magnetron sputtering.

The top surface of low-mobility films are generally rough, and often referred to as "cauliflowerlike,"[15] while the cross sections usually show a "columnar" structure which develops from a competition for growth of power-law-shaped cones ($y=x^n$, where y is the height of the cone, x the radius of the cone, and n the exponent). Such paraboliclike[16] cones, which represent the void network structure, result from clustering during the random ballistic aggregation process.

Recent works on plasma-enhanced chemical-vapor deposition of *a*-Si:H by Drevillon[17] and Collins and Cavese[18] using *in situ* ellipsometry showed that various degrees of void density gradients can exist at the substrate-film interface and are dependent on preparation conditions such as substrate temperature, ion bombardment energy, and ratio of inert gas to silane. Our experimental results combined with theirs tend to support the cone-growth competition model as opposed to pure columnar growth, where one would not expect such a large difference, if any, in the void content of the two sides of the film. Furthermore, the cones usually have smaller cones embedded inside of them due to the continual clustering which occurs in ballistic aggregation. This self-similar structure points to a fractal model of low-mobility thin-film growth.[19,20]

Deposition onto a transparent prism allows "post-*in situ*" ellipsometric diagnostics of the early growth stages where interesting information is stored on the film's void fraction and nucleation density. Image analysis of TEM micrographs can give us geometric parameters during the early growth, while the ellipsometric data will be used to model the density of the individual cones of various sizes.

This work was supported by the Air Force Office of Science Research under Contract No. AFOSR-84-0419, by the National Science Foundation under Grant No. DMR-8418160, and by the Philips and Dupont Optical Company.

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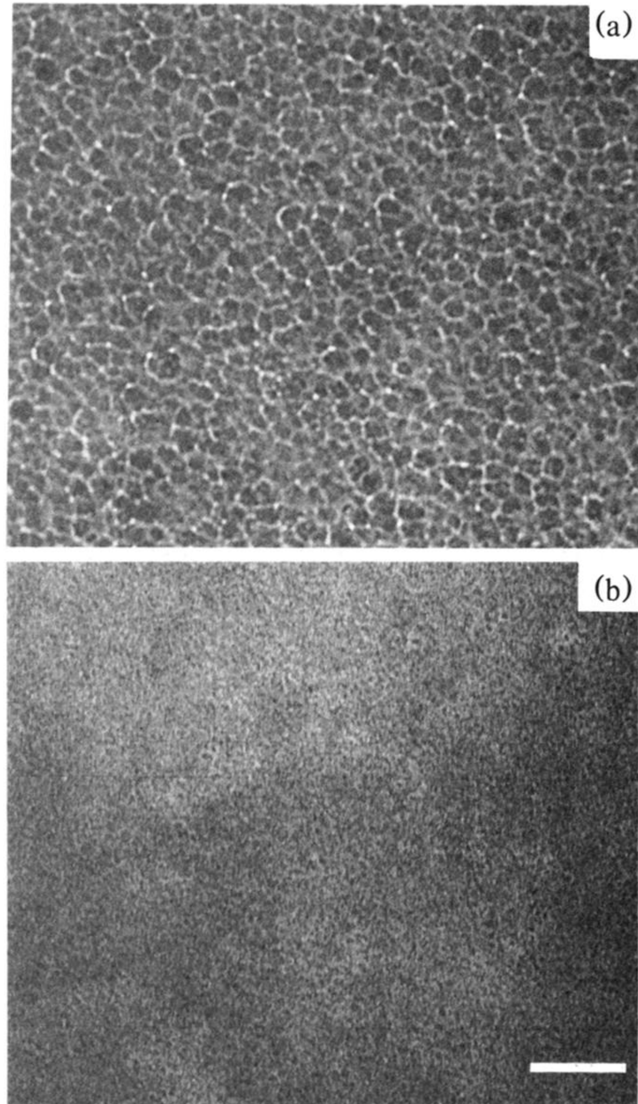

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