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Thickness dependence of optical gap and void fraction for sputtered amorphous germanium

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Amorphous germanium films 600 to 18 800 Å thick were deposited using rf-diode and dc-magnetron sputtering. Spectroscopic ellipsometry measurements were conducted on these samples over the photon energy range of 1.8–4.5 eV. These measurements were used to determine the void content of the deposited films. Transmission and reflectance measurements from 0.5–2.0 eV were used to determine the optical-absorption spectra. Tauc's plots were constructed and optical gaps extrapolated from these plots. A correlation was found between void-content and optical-gap values.

Variations in physical properties with film thickness have been reported for amorphous Ge, Si, and hydrogenated amorphous Si films deposited by glow discharge and rf-diode sputtering.[1–4] Changes in mass density, structure, optical, electrical, and photoelectrical properties with film thickness have been attributed to interface space charge effects,[1] microscopic grain-like or grain-boundary-like zone effects,[2] structural inhomogeneities at the film-substrate interface,[3] and a connected network of microcracks.[4] The existence of voids in films prepared by these methods has been noted in the literature for some time.[4–6] As is well established, the total volume of voids, their distribution, and connectivity can be varied by changing the deposition conditions such as substrate temperature and deposition rate. In addition, even with fixed deposition conditions there can be large variations in the void content as film thickness changes.[7]

The effects of voids on other properties of deposited films are not clearly understood.[8] This study examines the influence of the voids on the property known as the optical gap.[9] Films of amorphous germanium were deposited with thickness values from 600 to 18 800 Å. Spectroscopic ellipsometry was used to determine void content changes as film thickness increased. Transmission and reflectance were used to measure optical-absorption spectra. Tauc's[9] plots were constructed from the spectra and optical gaps were found by extrapolation from the plots.

Amorphous Ge films were prepared on Corning 7059 glass substrates using two different deposition systems. The systems chosen were rf-diode and dc-magnetron sputtering with polycrystalline Ge targets (99.999%). Deposition parameters for the films deposited using rf sputtering are described in the literature.[7] The dc-magnetron sputtering conditions were 500 V and 200 mA at an argon-gas pressure of 1 mTorr. Target to substrate distance was 27 cm.

The rf-diode films were prepared with thickness values of 600, 1800, 3500, 5000, 7400, and 11 000 Å. These thickness values were determined using a diamond-stylus profilometer instrument with 10% errors in film thickness as described elsewhere.[7] The dc-magnetron system films were deposited with thickness values of 700, 1000, 1600, 5000, 7900, and 18 800 Å.

Since the substrates were thermally floating an important parameter was the film temperature during deposition. For the rf-diode deposited films the surface temperature was measured with a thin-film thermistor and found to rise rapidly in the first 8 min (deposition time for the 600-Å film) from 23 °C to 50 °C and then approach an equilibrium value of 60 °C. The substrate temperatures using the magnetron deposition system were constant at 23 °C.

Spectroscopic ellipsometry measurements were performed at an incident angle of 70°. The photon energy range was ~1.8–4.5 eV, and within this interval it is estimated that the average probe depth is 500 Å. Precision and accuracy for these measurements are described in the literature.[10] The imaginary (ϵ_2) part of the pseudodielectric functions, calculated from the Δ and Ψ measurements on the films, are shown in Figs. 1 and 2. Figure 1 is a plot of the imaginary part of the pseudodielectric functions versus photon energy for films prepared using rf sputtering, while Fig. 2 shows the spectra for the dc-magnetron samples. The ϵ_2 values for the rf-sputtered films increase as film thickness changes from 600 to 7400 Å and then decrease for the 11 000-Å film. As indicated in Fig. 2, no systematic variations with film thickness occur for the magnetron samples, and the variations that are present represent film reproducibility limits.

Interpretation of these data in terms of differences in void fraction, surface oxide, and microscopic roughness of the films is described in detail in the literature.[7,10,11] Briefly, this procedure includes standard n-layer models, the Bruggeman effective medium theory, and regression analysis. Use of the Bruggeman model requires the dielectric function for nearly "ideal" amorphous germanium, a sample with minimum void fraction, microscopic roughness, and oxide overlayer thickness. As discussed in past studies, the dielectric function data of Connell, Temkin, and Paul[5] satisfy these criteria. The void content values of the rf and magnetron samples are relative to this selected reference and are defined as void fractions. Using

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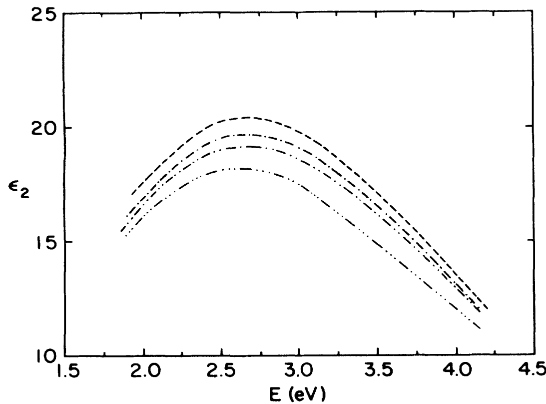

FIG. 1. Imaginary (ϵ_2) part of the dielectric functions vs photon energy [E (eV)] for rf-diode sputtered amorphous Ge films with thickness values of 1800 Å (three-dot dashed line), 3500 Å (two-dot dashed line), 5000 Å (one-dot dashed line), and 7400 Å (dashed line). The spectra for the 11 000-Å film overlap that for the 5000-Å film and are not shown.

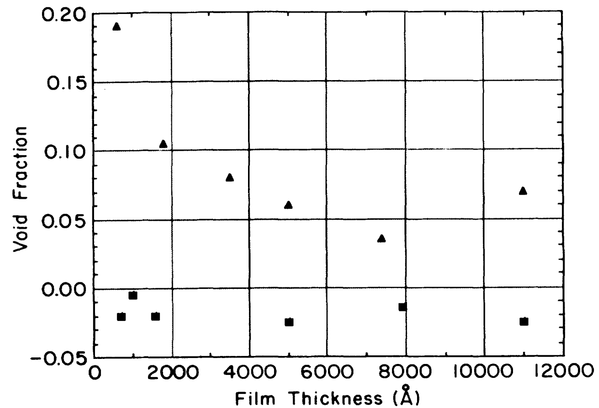

FIG. 3. Void fraction vs film thickness (Å) for rf-diode sputtered amorphous Ge films (triangles) and dc-magnetron sputtered films (squares). The dc-magnetron film with a value of 18 800 Å is placed on the thickness scale at 11 000 Å.

these reference data, the void fractions for the amorphous germanium films are summarized in Fig. 3. Slight differences due to substrate position were observed between the results on the c-Si (Ref. 7) substrates and the 7059 glass substrates used in this study.

Figure 3 is a plot of the void fraction versus film thickness for the rf-diode deposited films (triangles) and the dc-magnetron deposited films (squares). There is a large change in the void fraction as film thickness increases for the rf films, while the magnetron deposited films show no significant variation with thickness. For the rf-sputtered films the void fraction *decreases* as film thickness *increases* from 600 to 7400 Å. The void fraction then changes from a value of $\sim(3.5\pm0.7)\%$ for the 7400-Å film to $\sim(7.0\pm0.8)\%$ for the film with a thickness value of 11 000 Å. The film growth mechanisms responsible for the void distribution in these samples are not clearly understood.

Figure 3 also shows that *little* or *no* change in void fraction occurs as film thickness increases for the dc-magnetron samples. The void fraction values for the magnetron samples are also negative, which indicates that the density values are larger than that of the reference. However, the differences between the void fractions of the

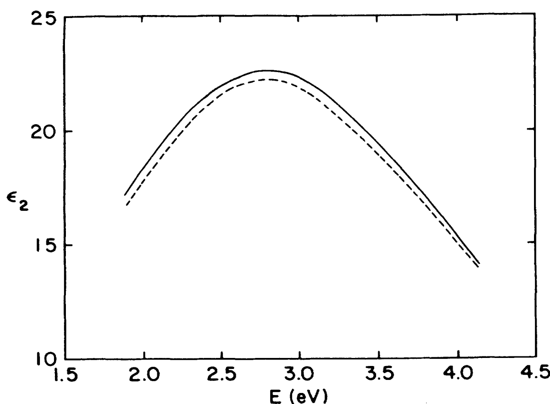

FIG. 2. Imaginary (ϵ_2) part of the dielectric functions vs photon energy [E (eV)] for dc-magnetron sputtered amorphous Ge films with thickness values of 1000 Å (dashed line) and 18 800 Å (solid line). Spectra for magnetron films with thickness values of 700, 1600, 5000, and 7900 Å all fall within the bounds shown in the figure.

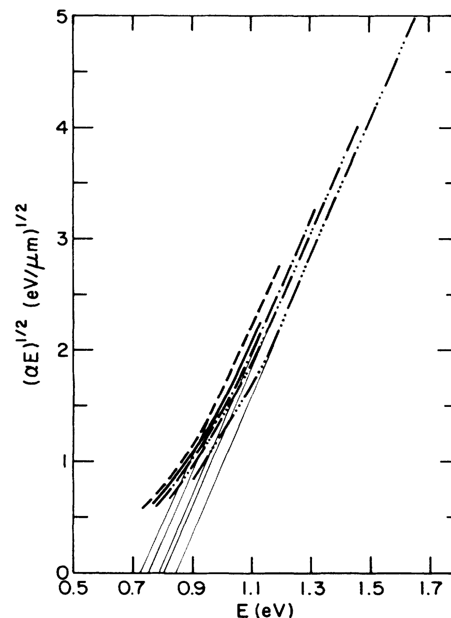

FIG. 4. Tauc's plot for rf-diode sputtered amorphous Ge films with thickness values of 1800 Å (three-dot dashed line), 3500 Å (two-dot dashed line), 5000 Å (one-dot dashed line), 7400 Å (dashed line), and 11 000 Å (solid line).

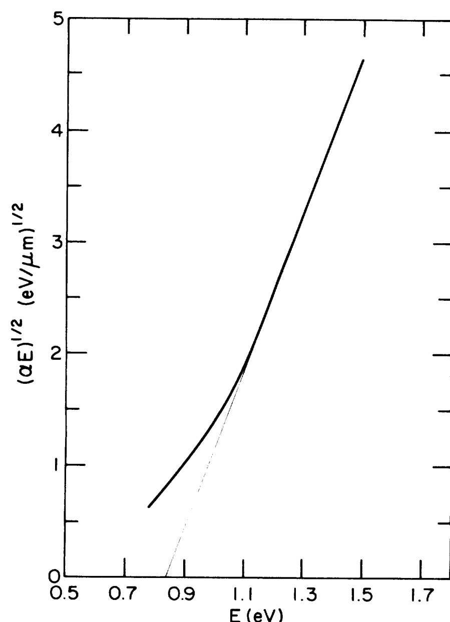

FIG. 5. Tauc's plot for dc-magnetron sputtered amorphous Ge films. The values for thickness between 1000 and 18 800 Å overlap and as such a solid line is drawn.

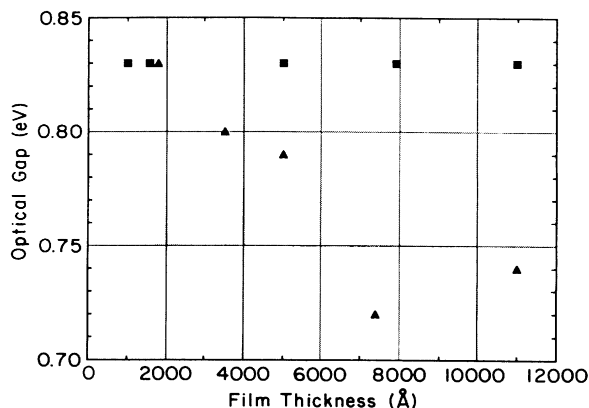

FIG. 6. Optical gap (eV) vs film thickness (Å) for rf-diode sputtered amorphous Ge films (triangles) and dc-magnetron sputtered films (squares). The dc-magnetron film with a value of 18 800 Å is placed on the thickness scale at 11 000 Å.

magnetron samples and the reference are small (-1 to 2%), and the pseudodielectric functions are essentially the same as that of Connell, Temkin, and Paul.[5]

The rf-sputtered and dc-magnetron samples thus consist of the same material in which there are large and variable changes in void content as well as no changes. Together they represent an excellent system to examine the influence of voids on other properties of the films. Therefore, following spectroscopic ellipsometry measurements and analysis, optical-absorption spectra for the films were determined from reflectance and transmission measurements using expressions described in the literature.[12]

The absorption spectra in Figs. 4 and 5, show the optical gaps as determined by Tauc's method.[9] The critical linear relationship between $(\alpha E)^{1/2}$ and E in the Tauc's plot lies above 1 eV, and this linear portion is extrapolated to yield the optical gap at $(\alpha E)^{1/2}=0$. Figure 6 is a plot of the optical gaps versus film thickness for the rf-sputtered films (triangles) and the dc-magnetron sputtered films (squares). The optical gaps for the rf samples *decrease* as film thickness values *increase*, from a value of 0.83 ± 0.01 eV for the 1800-Å film, to 0.72 ± 0.01 eV for the 7400-Å film, followed by a slight increase to 0.74 eV for the 11 000-Å film. The same figure shows *constant* values of 0.83 eV for the magnetron films.

In order to determine the presence of surface or bulk impurities, neutron-activation analysis and Auger and secondary-ion mass spectrometry were used as additional characterization techniques. Neutron-activation analysis on the samples revealed that the [Ar]/[Ge] atomic ratios *decreased* [$\sim$(2.2–0.8)%] as film thickness *increased* for the rf-deposited samples but were essentially constant ($<0.5\%$) for the magnetron films.[13] Secondary-ion mass spectrometry indicated that the impurity content of the films (other than argon) was minimal. Auger spectrometry combined with sputtering showed a surface layer consisting of carbon, oxygen, and germanium and no bulk impurities.

Comparison of Fig. 3 (where the void fraction is determined for the upper $\sim$500 Å) and Fig. 6 (where the optical gap is determined for the bulk or entire thickness) shows similar trends. For the rf-sputtered films, as the void fraction decreases the optical gap also decreases; this occurs for the films with thickness values from 1800 to 7400 Å. For the 11 000-Å film the void fraction increases slightly and there is a corresponding increase in the optical gap. The dc-magnetron samples show little or no change in void fraction and no differences in optical gap. The differences in optical band gap between the dc-magnetron films and the rf-diode films are possibly due to variations in the intrinsic effects (network structure) resulting from extrinsic effects (void content).

However, the possibility also exists that the presence of a graded void fraction influences the measured transmission and reflectance values such that interpretation of the resulting spectra in terms of a homogeneous film is no longer valid. Thus the contributions of intrinsic and extrinsic effects on the physical properties of thin films are difficult to experimentally separate and analyze. Additional experiments to investigate these contributions are in progress.

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