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Optical properties of pulsed laser deposited bismuth films

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Bismuth films are grown at room temperature onto Si substrates by pulsed laser deposition (PLD). Some films are deposited by dc sputtering (DCS) for comparison. PLD films are smooth and show micron-sized laminar grains as opposed to DCS films which are rough and show nanometer-sized columnar grains. The optical properties of the films have been studied by means of spectroscopic ellipsometry in the 300–800 nm wavelength interval over a period of six months. The results show that the refractive index of PLD Bi films is independent of the film thickness, thus providing reliable data of the optical constants of Bi films. In addition, it is shown that PLD films exhibit an improved stability to oxidation probably related to their favorable microstructural properties. The thickness dependence of the refractive index in DCS films is related to their surface roughness, the results being improved by pulsed laser melting of these films. © 1996 American Institute of Physics. [S0021-8979(96)01824-5]

I. INTRODUCTION

It has been reported that the optical properties of thin Bi films depend strongly on the film thickness¹ and it has been shown that only very thin films exhibit optical constants similar to those of bulk single-crystal Bi.^{2,3} This variation has been attributed to the microscopic surface roughness resulting from the columnar growth. To overcome this problem, films deposited onto heated substrates were studied since they show improved microstructural and surface characteristics.⁴ The film density was found to increase as the substrate temperature increased up to 70–80 °C, this increase also being related to a decrease in surface roughness. Films with the least surface roughness were produced at similar temperatures^{4,5} but their optical properties were studied over a nine-day aging period and the growth of a surface layer of bismuth oxide was found.⁵ It is most likely that surface roughness and oxidation are responsible for the large variation in the results, reported in the literature so far, for the optical constants n and k for Bi films. Therefore, there is a real need for reliable measurements of the optical constants of polycrystalline Bi films either by the development of *in situ* techniques, which may overcome the oxidation problems, or by the production of Bi films with improved structural properties and stability.

Polycrystalline Bi films have usually been prepared by thermal evaporation,^{1,4–7} although there are some reports on films grown by dc sputtering⁸ or the recently developed low-energy cluster beam deposition.⁹ The films grown on substrates held at room temperature are usually found to have columnar-like grains whose size increases as the film thickness increases.^{7,8} Abnormally thick columnar grains emerging from the surface, whose number and size also increase with the thickness of the films, have been found in both thermally evaporated¹ and dc-sputtered⁸ films leading to in-

creased surface roughness. Therefore, the higher the film thickness the higher the film roughness.

The aim of this work is to determine the optical constants of polycrystalline Bi films. We have used a recently developed technique, namely pulsed laser deposition (PLD), which has been proven to grow high quality films of complex materials. Its application to metallic thin films has been much more limited,^{10,11} but recently it has been shown that some PLD metal films exhibit special features when compared to films prepared by more conventional techniques.¹¹ To our knowledge, this is the first report on the deposition of Bi films by PLD.

The optical properties of the films have been studied by spectroscopic ellipsometry. The structural and optical properties of PLD films are compared to those grown by dc sputtering (DCS), both as deposited and after planarization by pulsed laser melting.⁸ Since different deposition techniques lead to films with different structure and surface roughness, their influence on the optical properties is discussed. Finally, aging effects have been studied by analyzing the change in the ellipsometric parameters over a period of several months.

II. EXPERIMENTAL DETAILS

The films were deposited onto Si (100) substrates held at room temperature, the target-substrate distance being 33 mm. PLD is performed by focusing an ArF laser beam [$\lambda=193$ nm, 12 ns full width at half maximum (FWHM), 5 Hz repetition rate] by means of a spherical lens (240 mm focal length) at 45° onto a rotating Bi (99.999%) target. The average energy density at the target site is calculated by integrating the energy density profile along its surface at an intensity of 0.1 of its maximum value as described elsewhere¹² and was fixed to ≈ 2 J/cm². The thickness of the films follows a distribution similar to that reported elsewhere for Ge¹³ and Bi¹⁴ films. It is uniform in a small area near the center of the deposited film where the characterization and optical measurements have been performed. The deposition time was in

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the range 250–1000 s and the background pressure of the system was 10^{-7} Torr. DCS films were grown in a dc magnetron sputtering system from the same target. The background pressure was 2×10^{-6} Torr and the operating Ar pressure was 4×10^{-3} Torr. The deposited film thickness was determined by Rutherford backscattering spectrometry (RBS) to be: 20, 40, 66, and 100 nm for PLD films and 30, 60, 100, and 200 nm for the DCS films.

Both PLD and DCS films of approximately 50 nm have also been grown onto carbon mica substrates in order to analyze the film microstructure by means of transmission electron microscopy (TEM). TEM specimens were prepared by floating the films off the mica in de-ionized water and picking them up on copper grids. They were analyzed in plan view in a Philips EM-420 transmission electron microscope. Surface analysis was performed using a digital 960 Zeiss scanning electron microscope (SEM).

Some of the DCS films were irradiated using an ArF excimer laser, in vacuum (1×10^{-5} Torr) and 24 h after deposition, in order to planarize them through a melting-rapid solidification process as reported elsewhere.⁸ The laser beam was passed through a homogenizer to obtain a homogeneous 4 mm $\times$ 4 mm beam at the sample site. A He–Ne probe beam ($\lambda = 633$ nm) pulsed to $\tau = 1$ μ s by means of an acousto-optic modulator was used to monitor the reflectivity changes during irradiation in real time. The specular reflectance of PLD and DCS films was determined both before and after irradiation by using a He–Ne laser beam and a calibrated piroelectric detector to measure both the incident and reflected energies.

The ellipsometric parameters, $\tan \psi$ and $\cos \delta$ were measured by means of a SOPRA spectroscopic rotating polarizer ellipsometer in the 300–800 nm wavelength range and using steps of 10 nm. The absolute errors of $\tan \psi$ and $\cos \delta$ are lower than 5×10^{-4} and 10^{-3} , respectively. The angle of incidence was $70.00^\circ \pm 0.05$. The ellipsometric parameters of some DCS and PLD films were measured several times over a period of six months. During this time, the specimens were stored at room temperature and at atmospheric pressure in a dust free environment.

III. RESULTS AND DISCUSSION

Figure 1 shows both the real n and imaginary k parts of the refractive index of PLD films. Results obtained from the four films of different thicknesses that were studied are all included. The optical constants have been calculated from the ellipsometric parameters assuming an absorbing film on a crystalline silicon substrate and using the thicknesses determined by RBS. The results clearly show that the refractive index of PLD films has no significant dependence on the film thickness and that the refractive index of the two thickest films are identical. Furthermore, these two films behave optically as a semiinfinite medium and the optical constants of the thickest film will be taken as a reference in the present work. The thicknesses of the thinner films can be determined from the ellipsometric parameters by assuming that the films have identical constants to the thicker films and the results are in excellent agreement with those determined from RBS measurements. The ellipsometric parameters of PLD films

FIG. 1. Real (n) and imaginary (k) parts of the refractive index of Bi, as a function of wavelength, obtained in PLD films of different thicknesses: (—) 100 nm, (+++++) 66 nm, (---) 40 nm, and (····) 20 nm. Results reported in the literature for Bi films [(Δ) Ref. 1 and ($*$) Ref. 6] and for bulk crystalline Bi [($\diamond$) Ref. 2 and ($\square$) basal plane and ($\circ$) optic axis in Ref. 3] are included for comparison.

were measured again after 26 h and no significant changes were observed. After two months, they were measured again and some differences were observed. The new parameters were then simulated by assuming a transparent oxide overlayer. Since the refractive index of Bi_2O_3 in the range 0.5–0.7 μm was found constant and equal to 2.56¹⁵ or varied between 2.3 and 2.5 at 0.63 μm ,¹⁶ a constant refractive index $n = 2.5$ has been assumed in the whole spectral range studied. Variations up to 10% in the refractive index of the oxide layer introduce similar variations in the thickness determined. The experimental results fit very well with an oxide overlayer whose thickness varies from 1.0 nm for the thinnest film to 1.5 nm for the thickest one. After five months, the results for the thickest films fit very well with a 2.0-nm-thick oxide overlayer, thus showing that the film surface is nearly passivated by the oxide overlayer. These results prove the higher stability of PLD films when compared to those reported elsewhere for 50-nm-thick films prepared by thermal evaporation⁵ (1–2-nm-thick oxide overlayer after 2–5 months in PLD films as opposed to 0.5–1.6 nm in evaporated films after 1–9 days).

Figure 1 also includes the refractive index reported in the literature for bulk single-crystal $\text{Bi}^{2,3}$ and thermally evaporated Bi films.^{1,6} It is clearly seen that the data reported in the literature show a high dispersion, although the general trend is similar in all cases including our PLD films. It is

worth noting that most of the k values reported in the literature are lower than those of our PLD films. To evaluate the optical density of PLD films, we have used an effective medium modelling method combined with a standard linear regression method¹⁷ to simulate the data reported in the literature for bulk Bi and thermally evaporated films. We have assumed that the material is formed by an homogeneous mixture of Bi and voids, using the refractive index of the thickest PLD film as a reference for Bi. The results show that PLD films are 11%–21% denser than the thermally evaporated films reported in Ref. 6 and bulk Bi.^{2,3} Nevertheless, when the same comparison is done to the data reported in Ref. 1 for films grown onto heated substrates, these films seem to be denser than our PLD films. Although the authors claim that the optical constants of these films are measured through the substrate to avoid surface roughness,¹ the films were too thin to neglect the effect of the film–air interface roughness. Furthermore, the validity of the optical constants from these back measurements was examined by the study of the dependence of the transmittance of different films at a single wavelength as a function of thickness. Since the resolution of the thickness and transmittance measurements was poor, the reliability of the optical constants reported in Ref. 1 is questionable.

The structural properties and surface morphology of PLD films, as studied by TEM and SEM, are shown in Figs. 2a and 3a, respectively. PLD films are homogeneous and composed of laminar crystals a few μm in size. The surface is smooth, although some particulates similar to those usually reported in PLD films could be found.¹⁸ However, as reported elsewhere for PLD Ge films,¹⁹ they seem to have no significant effect on the optical properties. The structural properties and surface morphology of DCS films are shown in Figs. 2b and 3b for comparison. DCS films show a columnar-like grain growth similar to that widely reported in the literature for Bi films^{4,7,8} with a grain size of 50–80 nm, which is notably smaller than that of PLD films. In addition, DCS films show a strong surface roughness, related both to the columnar growth and the presence of abnormally large grains (an example of which is marked with an arrow in Fig. 2b) which are more clearly visible in the SEM image in Fig. 3b. The surface roughness increases with the film thickness,⁸ similar to that reported earlier for thermally evaporated films.

The ellipsometric parameters measured in the DCS films show a strong dependence on the film thickness even for thicknesses greater than 100 nm, at which PLD films exhibited a semi-infinite medium behavior. Furthermore, two different 200-nm-thick films grown in similar conditions showed slightly different ellipsometric parameters. This thickness dependence and lack of reproducibility of the optical properties for similar thickness films is most likely related to the film roughness as shown by the TEM and SEM images included in Figs. 2b and 3b. As suggested in Ref. 4, we have simulated these rough films as a mixture of Bi and voids using the effective medium modelling method mentioned above. The resulting void fraction is included in Fig. 4 and it is clearly shown that the film density decreases as the film thickness increases and, as a consequence, roughness increases. This result is in very good agreement with our

FIG. 2. TEM images of approximately 50-nm-thick (a) as grown PLD films, (b) as grown DCS films, and (c) DCS films after laser irradiation with 1 pulse of 30 mJ/cm².

TEM and SEM observations and leads to the same conclusion as the results obtained when varying the substrate temperature during thermal evaporation.⁴ It is also worth noting that the density of DCS films is always lower (by at least 15%) than that of PLD films. The ellipsometric parameters of DCS films measured over a period of six months after film deposition showed variations which could not be explained in terms of a planar oxide overlayer growing at the surface.

In a recent work on laser irradiation of DCS Bi films,⁸ it has been reported that surface roughness decreases upon laser melting and consequently an increase of the film specular reflectance is obtained. Figure 5 shows the specular reflectance measured, at 633 nm, in PLD films and DCS films several weeks after deposition as a function of the film thickness, the results obtained in DCS films both before and after laser irradiation also being included. The specular reflectance of Bi films, calculated using the refractive index measured in

FIG. 3. SEM images of approximately 50-nm-thick (a) as grown PLD films, (b) as grown DCS films, and (c) DCS films after laser irradiation with 1 pulse of 30 mJ/cm².

the thickest PLD film at the same wavelength ($n=1.75$, $k=4.25$), is also shown to provide a reference for comparison. It is clearly seen that the reflectance of PLD films follows the calculated values very well and therefore shows no significant dependence on the film thickness, the slight shift in the experimental values most likely being related to the formation of a thin oxide overlayer. In DCS films, the reflectance decreases strongly as the film thickness is increased, the value for the thickest DCS film being close to 30% of the calculated one. Upon pulsed laser melting-rapid solidification, the reflectance of DCS films was observed to increase up to a saturation value as the number of pulses was increased.⁸ The reflectance of the films upon laser irradiation was thus measured once this reflectance increase was saturated which typically occurred for 1–3 pulses of energy density 90–120 mJ/cm². The enhancement of the film reflectance observed in Fig. 5 is mainly related to the increase in

FIG. 4. Void fraction of DCS films as a function of the film thickness in (□) as grown films and [(○), (△)] films after laser irradiation. The void fraction of the latter films is simulated (△) with and (○) without an oxide surface overlayer.

the grain size and the planarization produced in these films upon laser melting, as can be seen in the TEM and SEM images included in Figs. 2c and 3c. The films have laminar crystals (Fig. 2c) with a grain size comparable to that of PLD films (Fig. 2a) and a high density of voids. The SEM image (Fig. 3c) shows that the density of the abnormally large grains has been notably reduced.

The ellipsometric parameters measured in the DCS films after laser irradiation have been simulated using the same procedure as that followed for the as grown films. The irradiation conditions are similar to those described above for Fig. 5 and the calculated void fraction is also plotted in Fig. 4. In this case the void fraction depends very little on the film thickness and it is strongly reduced in the thickest film. This result is consistent with a decrease of roughness and is in agreement with the TEM and SEM observations. Nevertheless, upon irradiation the thinner films show a slightly higher void fraction than that of the as grown or irradiated thicker films. This result is unexpected since the highest planarization has been achieved for the thinner films. Although the irradiations are performed in a short time (48 h after deposition), surface oxidation of the as grown films cannot be completely ruled out. It has been reported that the oxide over-

FIG. 5. Specular reflectance of Bi films as a function of the film thickness for (△) PLD films and DCS films, both (□) as grown and (○) after laser irradiation. The continuous line corresponds to the specular reflectance calculated using the optical constants of PLD Bi films determined in this work.

layer thickness in films with a similar structure, i.e., columnar-like grains, is close to 1 nm after 48 h⁵ and these oxidation effects should be more important in the thinner films. Therefore, it is more realistic to assume that the irradiated films behave like a two layer system on a substrate: a thin (1 nm) oxide overlayer and a layer formed by a mixture of Bi and voids. The void fractions calculated with this model and using the optical constants given above for the oxide overlayer are also included in Fig. 4 and show that the density of the laser irradiated films is nearly independent on the film thickness. These results also show that, although the density of DCS films is greatly increased by laser irradiation, it is still at least 10% less dense than that of PLD films. The low density of the irradiated films, in spite of the clear increase in grain size and surface smoothness, is most likely related to the formation of many voids during the melting-rapid solidification process induced by the laser. These are evident in the TEM image included in Fig. 2c.

IV. CONCLUSIONS

Pulsed laser deposition produces Bi films with micron-sized laminar crystals, smooth surface and an improved stability to oxidation. The refractive index of these films in the 300–800 nm range is independent of the film thickness and the optical properties of aged films (over several months) can be well simulated by assuming a 1.0–1.5-nm-thick oxide overlayer. The optical properties of dc-sputtered films are found to depend strongly on the film thickness and this dependence could be minimized by pulsed laser irradiation which leads to improved microstructural (large laminar crystals as opposed to columnar crystals) and surface characteristics. The density of the irradiated DCS films is nevertheless 10% lower than that of PLD films due to the formation of many voids within the Bi crystals during the melting-rapid solidification process induced by laser irradiation.

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