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Spectroscopic ellipsometry of sputtered amorphous Ni$_{0.95}$Tb$_{0.05}$ and crystalline Ni

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Spectroscopic ellipsometry measurements have been performed on rf diode-sputtered films of crystalline Ni and the dilute amorphous alloy *a*-Ni$_{0.95}$Tb$_{0.05}$ for photon energies from 1.55–4.60 eV. The pseudo-dielectric-constants of crystalline Ni are found to be relatively similar to previous results obtained by other optical methods. The amorphous-alloy pseudo-dielectric-constant spectra exhibit a form qualitatively similar to that obtained by a broadening of the crystalline Ni spectra. The results thus suggest that the similar short-range order in the two phases and the predominance of *d*-electron transitions with local character result in the observed spectra correspondence.

INTRODUCTION

The short-range order (SRO) of amorphous metals often indicates qualitative similarities to crystalline metals, particularly in exhibiting approximately equal nearest-neighbor distances and high packing densities. The extent to which nonperiodicity and varying degrees of disorder modify the electronic properties of amorphous metals relative to crystalline systems is not, however, known in any detail. Photoemission measurements have generally shown the occupied valence-band density of states to be similar within the limited spectral resolution of 0.5–1.3 eV of the method.[1] Vibrational studies on crystalline transition-metal systems have shown the predominance of nearest-neighbor interactions in phenomenological force-constant models.[2] In pure amorphous transition metals, theoretical studies[3,4] have suggested that fluctuations in nearest-neighbor distances and interactions will modify the electronic and vibrational spectra relative to crystalline systems. In these studies, it has often been presumed that large variations in first-neighbor distances may occur in amorphous metals. Recent studies[5] in dilute *a*-Ni alloys suggest, however, a higher degree of SRO than often assumed. In particular, amorphous *a*-Ni$_{0.95}$Tb$_{0.05}$ radial distribution function (RDF) measurements indicate a spread of ~3% in values of the first-neighbor distances below the first Ni-Ni peak value. Very good agreement with a relaxed dense-packed model of von Heimendahl[6] for pure *a*-Ni was noted here. Density measurements have also indicated a packing fraction ~7% below that of *c*-Ni, but above the hard-sphere value of 0.637.

In this article, we report on spectroscopic ellipsometry measurements that probe the dielectric constants and joint valence- and conduction-band densities of states of this *a*-Ni alloy, as well as that of *c*-Ni. The spectra of crystalline Ni films prepared under similar sputtering conditions to the *a*-Ni$_{0.95}$Tb$_{0.05}$ alloy provide a direct comparison of ellipsometric data, as well as with existing *c*-Ni results obtained by other methods. In this manner, the influence of surface sensitive corrections to the pseudo-dielectric-constants may be estimated. The high sensitivity of spectroscopic ellipsometry to changes in the optical constants of metals, without the difficulties inherent in ultrathin-film transmission or Kramers-Kronig transformed reflectance measurements, favors this method for the study of amorphous metals.

Previous studies[5,7] of thin- and thick-film *a*-Ni$_{0.95}$Tb$_{0.05}$ indicate that this material is stable at room temperature. As such, this alloy provides a first approximation to pure amorphous transition metals that are normally unstable at room temperature. The reported pseudo-dielectric-constants and the dielectric spectra of the amorphous Ni alloy are found to exhibit a number of similarities with that of *c*-Ni, confirming the important role of SRO and the predominance of *d* states on the optical spectra for $\hbar\omega \sim 1.5$–5 eV.

EXPERIMENT

Thin films of 1000-Å thickness of *c*-Ni and *a*-Ni$_{0.95}$Tb$_{0.05}$ were prepared by rf diode sputtering from 2-in.-diam targets at a pressure of 11 mTorr in a system of base pressure 10^{-7} Torr. Substrates of crystalline Si were maintained near 300 K to yield homogeneous, amorphous thin films. Neutron-activation analysis on thin films indicated a composition equal to that of the sputtering target. Previous studies of thin films prepared under these conditions indicate that the films are dense, and have relatively smooth surfaces with little or no evidence of columnar microstructure. To form the amorphous alloy, the substrate platform was water cooled, while for the polycrystalline Ni film, it was left thermally floating in the plasma with no substrate cooling. This results in temperature rise of order $150 \pm 50\,^\circ$C typically for thin crystalline films on glass substrates. X-ray-diffraction measurements indicated the absence of detectable *c*-Ni in the amorphous alloy films.

Spectroscopic ellipsometry measurements at 300 K were obtained at a 70° angle of incidence for photon energies at 0.05 eV intervals in the range $\hbar\omega = 1.55$–4.60 eV. A rotating-analyzer configuration similar to that of Aspnes and Studna[8] was employed. The complex pseudo-dielectric-constants $\tilde{\epsilon}(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ were obtained from the conventional ellipsometric parameters

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Δ and ψ from the relation

$$\tilde{\epsilon}(\omega)=\sin^2\phi+[(1-\tilde{\rho})^2/(1+\tilde{\rho})^2]\sin^2\phi\tan^2\phi\,,$$

where $\tilde{\rho}=\tan\psi\exp(i\Delta)$ and ϕ is the angle of incidence. The pseudo-optical-constants $n(\omega)$ and $k(\omega)$ were evaluated from the relation $(n+ik)^2=\tilde{\epsilon}$.

As is well known, noticeable differences can arise between the pseudo-optical and actual dielectric constants due to the contributions of surface overlayers and/or surface roughness on the experimental samples. In general, it is difficult to ascertain the role of these contributions. In the present study, we have chosen the thin-film formation conditions to be such that the roughness contributions are minimized while still allowing the formation of the amorphous state. The fixed geometry and plasma conditions for both crystalline and amorphous materials, as well as the moderate temperature for c-Ni formation, are expected to yield similar degrees of roughness. To estimate the role of an oxide overlayer, we have calculated the correction to the evaluated pseudo-optical-constants for the case of a homogeneous ordered 10-Å thick layer of NiO. As noted in the data, the influence of this thin, relatively nonabsorbing layer is to similarly change the crystalline and amorphous spectra. As such, the differences observed between crystalline and amorphous samples is expected to be relatively well represented here, particularly in terms of the qualitative and semiquantitative changes in the dielectric spectra.

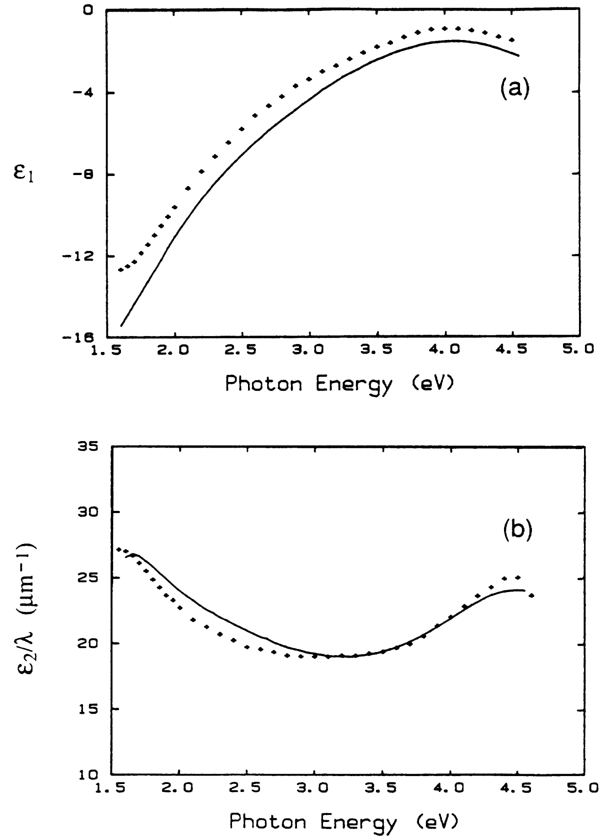

FIG. 1. Comparison of the (a) real and (b) imaginary parts of the pseudo-dielectric constants of rf diode-sputtered c-Ni (solid line) (this work), and corresponding values of polished c-Ni (filled diamond) (Lynch and Hunter, Ref. 9) from reflectance measurements.

EXPERIMENTAL RESULTS AND DISCUSSION

A comparison of the pseudo-dielectric-constants $\epsilon_1(\omega)$ and $\epsilon_2(\omega)/\lambda$ to the tabulated data of Lynch and Hunter[9] is shown in Fig. 1. The latter data were obtained from reflectance measurements on a polished c-Ni sample using the Kramers-Kronig transformation method. These workers did not attempt to correct for the thin layer of nickel oxide present on the surface and thus their results are appropriate for comparison with pseudo-optical data obtained in the present studies. As Fig. 1 indicates, the spectral variations are very similar for $\epsilon_2(\omega)/\lambda$, where the magnitudes agree within $\lesssim 5\%$. The form of $\epsilon_1(\omega)$ is also quite similar to that of Lynch and Hunter. The larger $|\epsilon_1(\omega)|$ observed here is due to somewhat larger $k(\omega)$ and smaller $n(\omega)$ values. The spectral form of these pseudo-optical-constants are, however, rather similar to that of Lynch and Hunter.[9] These small differences are typical of optical constant variations obtained by different methods, particularly on samples with different preparatory histories. Further, given the sensitivity of the Kramers-Kronig method to the extrapolation of the reflectance to inaccessible regions of the spectral range, these differences are not surprising.

The influence of a thin oxide layer on modifying the pseudo-optical-constants is shown in Fig. 2 for crystalline Ni. For simplicity, a homogeneous layer of crystalline NiO of 10 Å thickness was employed. As the results indicate, the artificial removal of such an oxide layer is rather small below $\sim$3.5 eV and results in a small decrease in $\epsilon_1(\omega)$ to more negative values. As this decrease is approximately constant in this range, the relative reduction is larger where $|\epsilon_1(\omega)|$ is small. Similarly, the correction for the thin oxide results in a nearly constant increase in $\epsilon_2(\omega)/\lambda$ to larger values, with $\Delta\epsilon_2/\lambda \simeq 2.5\ \mu\text{m}^{-1}$. Above the absorption edge at 3.8 eV of crystalline NiO, the correction results in a change in shape of the dielectric spectra. As previous data do not exhibit this behavior and the role of roughness is expected to be relatively monotonic with energy, the presence of a shape change is interpreted as a limitation of an assumed uniform NiO layer model. Further, the crystalline oxide layer is likely to be nonstoichiometric with a composition NiO_x. Evidence for such disorder is present in interference-enhanced Raman scattering studies of c-Ni trilayers, which exhibit first-order Raman scattering which would not be allowed for an ordered NaCl structure for NiO. It is reasonable to expect that the effect of this disorder is to smooth the spectra near the ordered c-NiO absorption edge, thus removing the feature at $\sim$3.8 eV that arises from gap absorption. Optical absorption measurements on NiO_x with $x>1$ clearly indicate that this peak is substantially modified in a manner consistent with the current results.[10] The influence of a thin oxide layer on the pseudo-dielectric-constants of a-$\text{Ni}_{0.95}\text{Tb}_{0.05}$ is similar to that of c-Ni.

A comparison of the real and imaginary parts of the

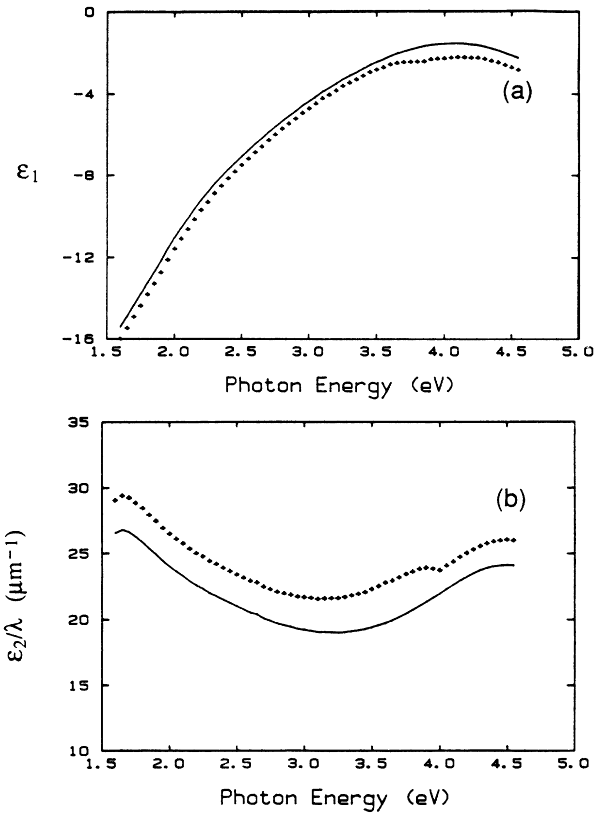

FIG. 2. Effect of a homogeneous 10-Å film of NiO on measured pseudo-dielectric-constants as measured in this work (solid line), and calculated effect of removal of 10-Å NiO film (filled diamond). (a) ϵ_1 and (b) ϵ_2/λ.

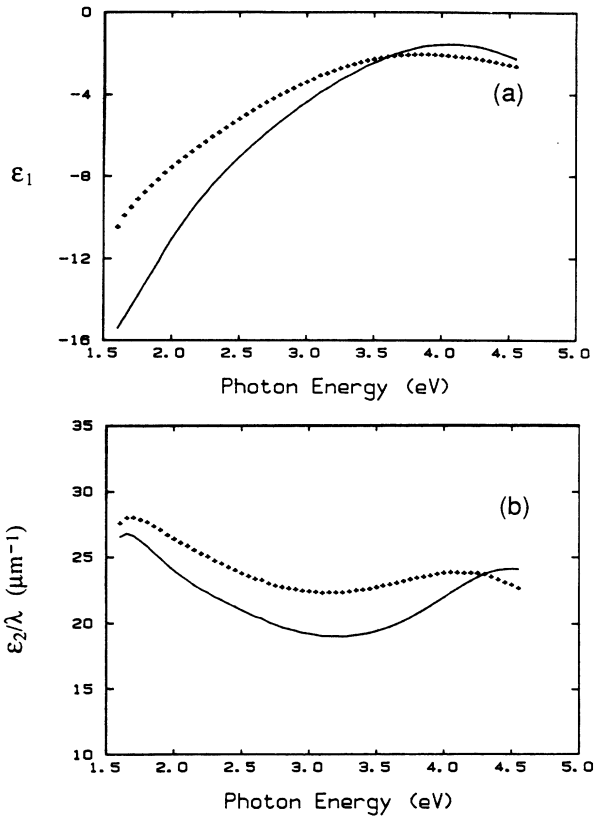

FIG. 3. Comparison of the real and imaginary parts of the pseudo-dielectric constants (a) ϵ_1 and (b) ϵ_2/λ of *c*-Ni (solid line) and *a*-$\mathrm{Ni_{0.95}Tb_{0.05}}$ (filled diamond).

pseudo-dielectric-constant spectra of *c*-Ni and *a*-$\mathrm{Ni_{0.95}Tb_{0.05}}$ is shown in Figs. 3(a) and 3(b). Given the broad structureless background in $\epsilon_2(\omega)$, the differences in the imaginary part are enhanced in the $\epsilon_2(\omega)/\lambda$ spectra shown in Fig. 3(b). As Figs. 3(a) and 3(b) illustrate, the qualitative form of the amorphous and crystalline spectra are rather similar. These differences and similarities in form are independent of small oxide contributions such as those estimated in Fig. 2. The major low- and higher-energy features in ϵ_2/λ at $\sim$1.7 eV and 4.5 eV of *c*-Ni exhibit parallels in the amorphous alloy. The broader nature of the latter spectra are reasonable to attribute to short-range order fluctuations, particularly variations in the distribution of first neighbors. The observation of a 3% width to the lower portion of the first peak of the RDF of *a*-$\mathrm{Ni_{0.95}Tb_{0.05}}$, as well as larger radial broadening at higher distances are a logical origin for the changes in $\epsilon_2(\omega)$ between crystalline and amorphous spectra. Similar effects of broadening of the higher-energy peak have been observed[11] in the $\epsilon_2(\omega)$ spectra of alloys of *c*-Ni with other transition metals. In this case, however, the fluctuations in interatomic potential are primarily due to atomic site variations, although some structural relaxation effects may also occur.

The shift of the peak in ϵ_2/λ of $\sim$0.3 eV of the amorphous alloy to lower energies along with the observed broadening is comparable to the effects of disorder on the *d* bands of Cu and Ni in the solid to liquid (*l*) transition.[12] While the *l*-Ni results do not allow a precise peak in ϵ_2/λ to be determined, the *l*-Cu data indicate a shift of $\sim$0.3 eV that are a consequence of changes in the valence *d* bands upon melting.[13] Structural studies of the liquid state indicate similar SRO for Cu and Ni.[14] In addition, the changes in the form of the RDF are similar to those observed in *a*-$\mathrm{Ni_{0.95}Tb_{0.05}}$.[5] In particular, the decrease in coordination number and asymmetric broadening of the first RDF peak to larger distances are observed. This suggests that the observed changes in the peak and form of ϵ_2/λ of Fig. 3 are primarily due to the increased disorder within the first coordination sphere. If the SRO is not similar between the amorphous and crystalline states, the form of ϵ_2/λ in terms of shape and the positions of maxima and minima would be substantially different. Further, for electronic state calculations of *a*-Ni and *l*-Ni, different structural models are required, however, to determine the precise influence of changes in short-range structural distribution functions. The influence of longer-range, intermediate-range order variations are expected to be of less significance, given the dominance of SRO effects on both the electronic and vibrational states of *a*-Ni.[3]

Implicit in this discussion is a neglect of possible Tb contributions to the optical spectra. Photoemission measurements on amorphous transition-metal–rare-earth alloys indicate that the primary contribution of Tb is at lower binding energies, below the Ni *d*-band states. As such, direct Tb contributions to the dielectric spectra are expected to be small for the energy range studied. Some indirect effects of the Tb on the SRO about Ni atoms cannot be completely excluded, however. The spectral variations of $\epsilon_1(\omega)$ of Fig. 3 are also consistent qualitatively with a disorder-induced broadening from the c-Ni spectrum due to SRO structural variations. The more rapid decrease of ϵ_1 with energy of c-Ni is similar to that observed relative to liquid Ni.[12] For transition-metal systems both intraband Drude-like and interband processes contribute to the amorphous and crystalline spectra at lower energies of ≤ 0.3 eV.[15] The influence of intraband contributions is generally larger in $\epsilon_1(\omega)$. Thus, the more rapid decrease of ϵ_1 in c-Ni at lower energies $\lesssim 1.9$ eV may , in part, be a consequence of larger intraband contributions in c-Ni.[16] Although c-Ni and noncrystalline Ni phases are not free electronlike metals,[17] the qualitative influence of intraband effects may be noted from the simple Drude model. Here, for relatively fixed carrier concentrations and effective electron mass, a more rapid decrease in ϵ_1 occurs due to the larger collisional time. For liquid Ni or the amorphous alloy this is of order 10–15 times greater than c-Ni at room temperature.

The similarities of c-Ni and a-$\mathrm{Ni}_{0.95}\mathrm{Tb}_{0.05}$ dielectric spectra are in accord with d electron states dominating the valence and conduction bands for the energy transitions explored here. Preliminary, low-resolution (1.2 eV) x-ray photoemission spectroscopy measurements on sputter-cleaned films indicate very similar d bands for these materials.[18] The spectroscopic ellipsometry results thus suggest that the conduction-band states and optical matrix elements that enter the dielectric spectra are likely to be also similar in character. The spectra for c-Ni also indicate that transitions throughout the Brillouin zone are significantly contributing to the optical spectra, given that in the amorphous alloy no restrictions due to crystal momentum conservation exist. The presence in c-Ni of relatively flat d-band final states near or above the Fermi energy are the simplest means for understanding the relation between the amorphous and crystalline spectra. Energy-band calculations for c-Ni support this qualitatively.[19] Similarly, the density of states of a-Fe and a-Ni emphasize the dominant d-state contributions for the energy interval studied here. Theoretical studies[20] of a-$\mathrm{Ni}_{0.85}\mathrm{P}_{0.15}$ also indicate that the joint density of states is dominated by Ni d-band transitions for low to intermediate energies. In addition, the form of the joint density of states is found to be qualitatively similar to that obtained here from the ϵ_2/λ^2 spectrum of a-$\mathrm{Ni}_{0.95}\mathrm{Tb}_{0.05}$.

In summary, spectroscopic ellipsometry measurements of the concentrated Ni alloy with 5% Tb yield pseudo-dielectric-constant spectra that are very similar to that obtained from c-Ni by a disorder associated broadening. This is logically a consequence of a related short-range order about Ni atoms in amorphous and crystalline materials in which the predominant contributions to the dielectric function arise from d-band transitions near the Fermi energy. More detailed measurements of the conduction-band density of states would be useful to determine the extent to which the individual d bands are modified by disorder.

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