PICOSECOND ULTRASONICS STUDY OF Mo_xNi_{1-x} SOLID SOLUTIONS

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Abstract

We present in this work measurements of the elastic properties of metastable Mo_xNi_{1-x} solid solutions by picosecond ultrasonics, as a function of the alloy composition x. The samples, with a thickness of a few hundreds of nm, were obtained by ionic co-pulverization of Mo and Ni on silicon substrates. We used the picosecond ultrasonics technique, with an interferometric detection, to determine the longitudinal elastic constant C_{33} for the whole Mo fraction range ($0 < x < 1$). A softening of the elastic modulus C_{33} is observed for $0.28 \leq x \leq 0.73$; this mechanical instability is associated with a crystal/amorphous transition. Beyond this mechanical study, we also analyzed the dependence of the echo shape according to the sample's composition. The determination of the optical reflectivity change by an interferometric detection allowed the derivation of various parameters such as the complex refractive index and a complex photoelastic constant of the alloy. Analyzing the echo shape, we also put in evidence that the adhesion between the alloy and the substrate is not perfect.

Introduction

It has been demonstrated [1] that using very short laser pulses and a pump/probe technique, it's possible to generate picosecond acoustic pulses, which can be detected measuring the reflectivity change they induce on the sample surface ($\Delta r/r_0$). Later on [2], [3], it has been proposed to detect these short acoustic pulses using interferometric techniques which allow the simultaneous measurement of the real and imaginary parts of the optical reflection coefficient change. Picosecond ultrasonics and Brillouin Light scattering have been used to measure the elastic properties of various metallic multilayers and a softening of the effective elastic constant has been reported [4], [5]. From a phenomenological point of view, this softening can be ascribed to an interfacial zone exhibiting anomalous elastic properties. Stresses, disorder, or amorphization could be involved in the softening of the interfacial zone. In this paper, we studied metastable Mo/Ni solid solutions where an amorphous region between 28% and 73% of Molybdenum has been observed. We measured the longitudinal elastic modulus of these solutions using picosecond ultrasonics. Furthermore, analyzing the echo shape, we deduce optical parameters such as complex optical index and photoelastic constants.

Picosecond acoustics

We use a Ti:sapphire laser with a 750 nm wavelength, a 130 fs pulse duration and a 82 MHz repetition rate. A first light pulse (the pump), modulated at 1 MHz, hits the sample's surface, where its absorption creates a localized thermal stress which, in turns, gives rise to a short acoustic pulse. This wave propagates within the layer, is reflected on the substrate and comes back to the surface where it's detected by a time delayed laser pulse (the probe). The acoustic wave modifies the reflected probe pulse : on the one hand, there is a displacement of the sample surface which contributes to the phase of the reflected electromagnetic field ; on the other hand the strain pulse perturbs the sample dielectric constant which gives a contribution to both the amplitude (P) and the phase (Φ) of the reflected electromagnetic field. For small strain, the relative change of reflectivity can be written as $\frac{\Delta r(z,t)}{r_0} = P + i\Phi$. Both parts can be simultaneously measured with an interferometric detection [2].

Samples description

Mo/Ni solid solutions have been deposited using cathodical co-pulverization. Mo_xNi_{1-x} solid solutions (covering the whole range of molybdenum fraction x) samples were elaborated at room temperature (RT) using a high-vacuum (base pressure $\leq 10^{-8}$ Torr) sputtering apparatus equipped with a RF-plasma ion gun. They were grown on natural-oxydized (001) Si sub-

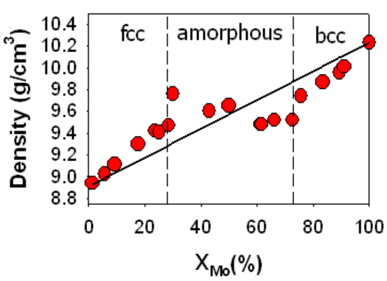

Figure 1: Density of Mo/Ni samples. Filled circles represent density x-ray measurements and the solid line gives the density derived from Mo and Ni fractions.

strates using a 1.2-kV accelerated Ar ion beam and with a deposition rate lower than 1 $\AA.s^{-1}$. The densities of each sample are shown on Figure 1. These thin solid films have a thickness of a few hundreds of nanometers ($150 \leq e \leq 300$ nm) making possible SONAR experiments with picosecond ultrasonics. An amorphous region is observed thanks to X-ray diffraction (XRD) for $28\% < x < 73\%$ in between a fcc region ($x < 28\%$) and a bcc region ($x > 73\%$).

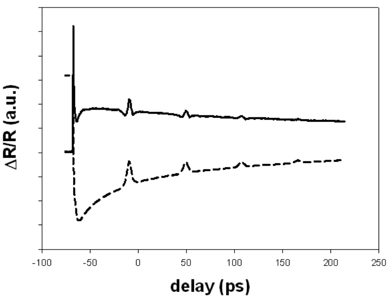

Figure 2: Reflectivity measurements. Real and imaginary parts are respectively plotted in solid line and dashed line.

Results and discussion

Typical reflectivity measurements are shown on figure 2. The longitudinal sound velocity is derived from the measurement of the time of flight between echoes. Results are reported on figure 3a. The longitudinal elastic constant $C_{33} = \rho v^2$ is dispayed on figure 3b. A softening of 25% of the C_{33} constant in the amorphous region is observed compared to the values of pure nickel or molybdenum. This behavior is very comparable to the C_{44} transverse elastic modulus measured by Brillouin Light Scattering (BLS) by Abadias et al [5] (figure 3b). This result indicates that if inter-diffusion processes occur at the interfaces in Mo/Ni multilayers, this

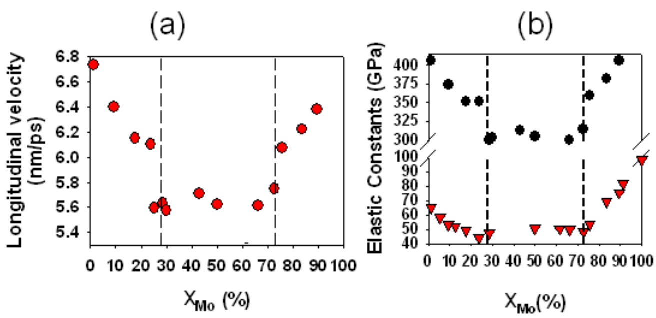

Figure 3: (a) - Longitudinal velocity in Mo/Ni samples versus Molybdenum fraction x. (b) - Elastic constants of Mo/Ni samples. C_{33} constants (circles) are measured by picosecond ultrasonics and C_{44} (triangles) by BLS experiments.

amorphization effect could explain the softening of the Mo/Ni multilayers elastic constant.

Echoes shape variation

Beyond the time of flight measurements, the acoustic echo shape dependence in terms of concentration appeared very interesting in this system. Large differences have been obtained for different concentration as shown on figure 4. In pure metals, the energy deposited

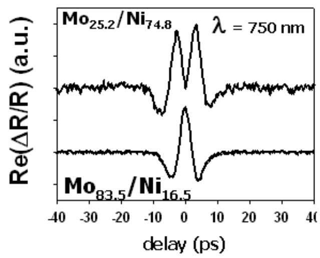

Figure 4: Echoes shape for 2 different compositions of Mo/Ni samples.

by the laser pulse absorption is very rapidly spread out by electronic diffusion and the duration of the acoustic pulse which is generated is usually larger than could be expected without diffusion. In alloys, the electronic diffusion is much less efficient than in pure metals and in a first step can be neglected to analyze the echo shape. Since the laser spot on the sample is much larger than acoustic propagation distances, a one-dimensional model can be considered ; furthermore, the material is assumed to be isotropic. Under such conditions, it can be shown [6] that the strain pulse propagating in the film writes

$$\eta(z,t) = -\frac{\eta_0}{2} sgn(z - vt)\, e^{-\alpha|z-vt|} \qquad (1)$$

where $\alpha = \frac{4\pi n''}{\lambda}$ is the optical absorption, v the sound speed, and η_0 a dimensionless parameter ; n'' is the imaginary part of the optical index $n = n' + in''$. This pulse is reflected at the interface with the substrate with the reflection coefficient $r_0 = \frac{Z_s - Z}{Z_s + Z}$, assuming a perfect interface ; Z and Z_s are respectively the film and the substrate acoustic impedances. When it reaches the free surface it gives a surface displacement

$$u(z = 0,t) = -\frac{\eta_0 r_0}{\alpha} e^{-\alpha v|t|} \qquad (2)$$

which modifies the phase of the reflected electromagnetic probe beam

$$\varphi = 2k_0 u(z = 0,t) = -\frac{\eta_0 r_0}{n''} e^{-\alpha v|t|}. \qquad (3)$$

Furthermore, the dielectric properties of the film are affected by the strain pulse through the photoelastic effect. The contribution to the photoelastic effect is given by

$$\left.\frac{\Delta r(z,t)}{r_0}\right|_{ph} = ik_0 \frac{\partial n}{\partial \eta} \frac{4n}{1-n^2} \int_0^{+\infty} \eta(z,t)\, e^{2ik_0 nz} dz \quad (4)$$

where $\frac{\partial n}{\partial \eta}$ is related to the dielectric and photoelastic constants. $\left.\frac{\Delta r(z,t)}{r_0}\right|_{ph}$ contributes both to the real and imaginary parts of the whole reflectivity change. Combining equations 2 and 4, we obtain the expressions of the real and imaginary parts $\frac{\Delta r(z,t)}{r_0} = P + i\Phi$.

$$\Phi(t) \propto e^{-\alpha v|t|} \left[1 + \gamma\Big(\cos(\beta+\theta) + r\sin(\beta+\theta) - \cos\theta\Big)\right]$$

$$P(t) \propto \gamma e^{-\alpha v|t|} \left[r\cos(\beta+\theta) - \sin(\beta+\theta) + \sin\theta\right] \quad (5)$$

where $\gamma e^{i\theta} = \frac{2nn"^2}{n'(1-n^2)(2n-n')} \frac{\partial n}{\partial \eta}$, $\beta = r\alpha v|t|$ and $r = \frac{n'}{n"}$.

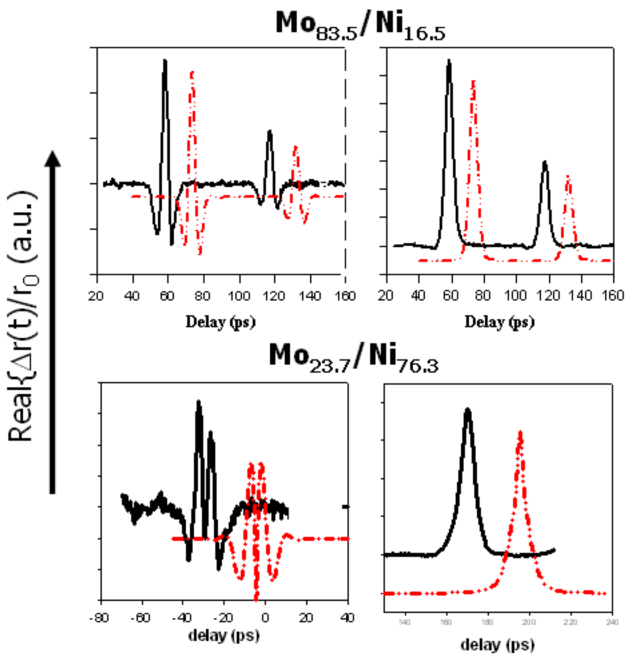

Figure 5: Echo shapes for 2 Mo Fractions : solid lines (experiments), dashed line (best fit). The fit curves have been shifted for a better visualization.

For the whole alloy series, γ appears to be in between 5 and 20%, which means that the Φ signal is almost proportional to $e^{-\alpha v|t|}$; thus $n"$ can be obtained in a very straightforward way from Φ. These values are reported on figure 6 and are in the range of the values of bulk molybdenum and nickel ($n"_{Mo} = 3.46$ and $n"_{Ni} = 4.25$ [7]). Hence, it seems to be reasonable to neglect the electronic diffusion and the acoustic attenuation for such alloys. Both parts P and Φ are fitted simultaneously by equations 5 to obtain n and $\frac{\partial n}{\partial \eta}$. As can be seen on figure 5, these simple expressions match very well the shapes of P and Φ whatever the composition of the sample is. The fitted parameters are reported

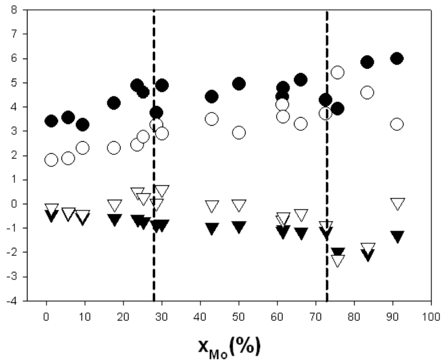

Figure 6: Real (filled patterns) and imaginary (clear patterns) parts of optical index (circles) and photoelastic coefficients (triangles) for the whole x range.

on figure 6 and exhibits only slight variations. The fitted shapes of the real parts are reported on figure 7 for a large concentration range. It's interesting to notice that the echo shape undergoes quite large changes with only small variations on the optical parameters. This high sensitivity of the echo shape to the optical parameters has already been studied on a single metallic film varying the probe wavelength [8].

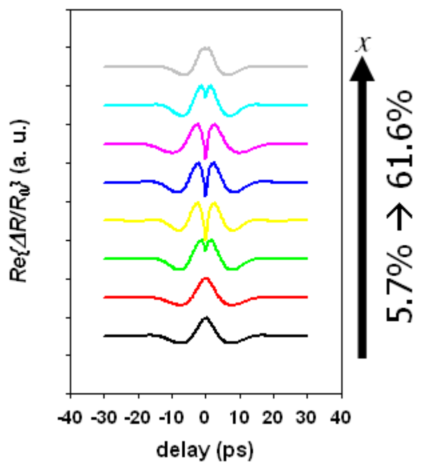

Figure 7: Evolution of the echo shape for a large range of Mo fraction.

Layer/substrate adhesion

In many samples, the real shape is not symmetrical, as can be seen on figure 5. this dissymmetry could be due to electronic diffusion but in that case, we would expect a step between the baselines on the both sides of the echo on the imaginary part Φ ; such a behavior is not observed. Thus, we tried to explain this asymmetry assuming a non perfect interface between the alloy sample and the silicon substrate. In that case, the boundary condition for the displacement has to be written $\sigma = \varepsilon^{-1}(u_{lay} - u_{sub})$, where ε^{-1} plays the role of a force constant between the film and the substrate [9]. With this new boundary condition, the reflection coefficient r_{ac} becomes frequency dependent,

$$r_{ac} = \frac{r_0 + i\omega\tau}{1 - i\omega\tau} \quad (6)$$

where $\tau = \varepsilon \frac{Z_{lay} Z_{sub}}{Z_{lay} + Z_{sub}}$. The low frequencies undergo normal reflection and high frequencies are totally reflected. The consequences of the imperfect interface on the echo shape is controlled by a dimensionless parameter $\delta = \alpha v \tau$ (later called the adhesion parameter) ; $\delta = 0$ for a perfect rigid interface. The shape distortion calculated for different δ values is displayed on figure 8. We tried to analyse the echo shape asymmetry on a

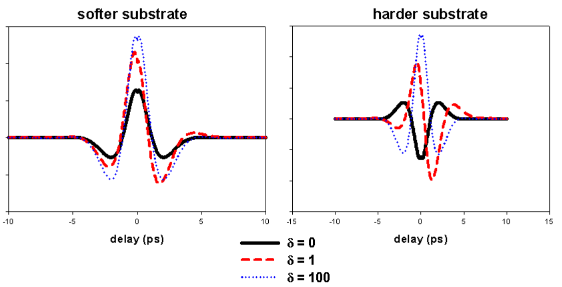

Figure 8: Influence of adhesion parameter δ on the real part P of the reflectivity change. For a softer substrate (a) and a harder one (b).

few samples using this simple model. The best fit obtained for the $Mo_{.835}Ni_{.165}$ sample is given on figure 9 ; for the value $\delta = 0.33$ it can be seen that the simulation

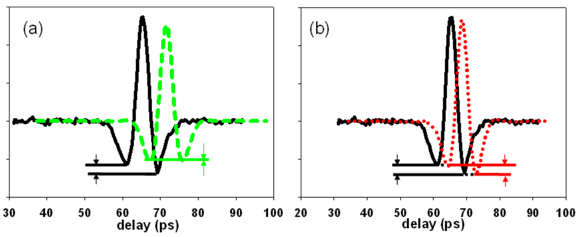

Figure 9: Echo shape (P) in the $Mo_{.835}Ni_{.165}$ sample. Solid lines represent experimental measurement. (a) - the dashed line is a fit assuming a rigid interface ($\delta = 0$). (b) - the dotted line is a fit for a non-rigid interface ($\delta = 0.33$).

matches quite well the echo shape. To be sure that the adhesion is the real source of the asymmetry, it could be useful to experimentally control and modify the δ value.

Conclusion

In this work, we measured longitudinal velocities and C_{33} elastic constants in Mo_xNi_{1-x} solid solutions. A softening of 25% has been observed for the concentration range corresponding to the amorphous region. This amorphization may be responsible of the effective elastic constant softening in Mo/Ni multilayers where amorphous interfacial zones could exist. Furthermore, optical parameters n and $\frac{\partial n}{\partial \eta}$ have been measured thanks to a simultaneous analysis of the echo shapes on the real and imaginary parts of the transient optical reflection coefficient. A small asymmetry in the echo shape, observed in a few samples, has been temptatively attributed to a slight adhesion defect on the silicon substrate.

References

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