Au diffusion in amorphous and polycrystalline Ni_{0.55}Nb_{0.45}

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(Received 8 April 1982; accepted for publication 26 May 1982)

Diffusion of Au in amorphous and polycrystalline Ni_{0.55}Nb_{0.45} has been studied by Rutherford backscattering spectroscopy of heat-treated Au/NiNb couples. The diffusion process is characterized by interdiffusion of Nb and Au with NiNb showing a Au miscibility of ~ 20 at. %. The Au diffusion coefficient in polycrystalline NiNb at 400 °C was found to be 1.6×10^{-15} cm²/s. The diffusion coefficient for Au in amorphous NiNb was found to be substantially less, $\sim 10^{-21}$ cm²/s at 400 °C. These results support the concept of using amorphous films as metallizations or diffusion barriers in high-temperature solid-state device applications.

PACS numbers: 66.30Jt

I. INTRODUCTION

The use of amorphous metal films either as primary metallizations or as diffusion barriers in high-temperature solid-state device applications was first suggested by Wiley *et al.*^{1,2} in 1981. The rationale behind this idea was quite simple: even at a relatively high device temperature of ~ 500 °C, the primary atomic transport mechanism in most metal-metal or metal-semiconductor coupled systems is grain boundary diffusion. Because amorphous metals have no grains, these films should undergo significantly less interdiffusion with their surroundings and therefore retain their integrity for much longer periods of time than would polycrystalline films. It is also thought that these amorphous metal films will be more resistant to electromigration, again because of the suppression of atomic motion along grain boundaries.³ The increased resistance to interdiffusion of an amorphous metal metallization should have a direct bearing on the useful life of solid-state devices because most failures can be traced to problems with metallizations.⁴

In this initial report we present data and analysis of the interdiffusion between amorphous and polycrystalline NiNb films and thin Au overlayers. Amorphous NiNb (*a*-NiNb) is one of several proposed high-temperature solid-state device metallizations under investigation. Au was chosen as the overlayer material both because its high mass facilitates the use of Rutherford backscattering analysis and because of its technological importance.

II. EXPERIMENT AND RESULTS

The *a*-NiNb films were deposited by rf sputtering onto single crystal Si substrates.⁵ The thickness of these films was ~ 1 μ m and the composition was 55 at. % Ni and 45 at. % Nb as measured by electron microprobe techniques. The crystallization temperature of NiNb was determined to be ≥ 600 °C by annealing the samples isochronally (1 h) over a range of temperatures from 400–700 °C, with the crystallinity of the films monitored after each anneal by x-ray diffrac-

tometry. For the interdiffusion measurements, a 200-Å Au layer was vacuum evaporated onto the surface of each *a*-NiNb film after a methanol rinse. In order to study the interdiffusion between the Au overlayer and the amorphous NiNb film, it is obvious that the sample temperature could not exceed the NiNb crystallization temperature of ~ 600 °C. Although this is a very high temperature for solid-state device operation, it is a difficult temperature range in which to study diffusion; for example, the diffusion length of Au in crystalline Ni at 600 °C is only 1 Å in a time of 1 s. In order to study interdiffusion at this and lower temperatures, one therefore requires a technique sensitive to internal atomic motion on an atomic scale. Ion beam analysis has previously been used successfully to study atomic diffusion in amorphous metal systems^{6–9}; the experimental technique used here is similar to that described by Chen *et al.*⁶

We used Rutherford backscattering (RBS) of 6-MeV α particles to simultaneously obtain concentration versus depth profiles of all three atomic constituents (Ni, Nb, and Au) in the near surface region of the Au/*a*-NiNb samples. By tilting the surface normal of the samples at an angle of 65° with respect to the incident beam direction and detecting the backscattered α particles at 165°, a depth resolution of < 50 Å (FWHM) at the Au/NiNb interface was obtained. This geometry is similar to that suggested by Williams and Moller.¹⁰

Three representative RBS spectra for Au-coated NiNb samples are plotted in Fig. 1. The upper histogram is for a virgin, unannealed sample, the middle for a polycrystalline NiNb sample annealed at 400 °C for 30 min, while the data plotted at the bottom are for an amorphous NiNb sample annealed 2 h at 550 °C. The polycrystalline Au/NiNb sample was prepared by annealing an amorphous NiNb sample at 650 °C (well above the crystallization temperature of 600 °C) for 1 h prior to evaporating the thin Au layer. For the unannealed sample, the surface edges of Au and the interface edges of Au, Nb, and Ni are readily evident. After the anneals, Au was observed to diffuse into the NiNb film, while Nb diffused into the Au overlayer. It is also apparent from Fig. 1 that the yields from Ni near the interface are lower after the anneals. This decrease is caused not by a smaller

^{a)}This work performed at Sandia National Laboratories supported by the U.S. Department of Energy under contract number DE-AC04-76DP00789.

FIG. 1. Typical α backscattering spectra for as-deposited Au/NiNb (upper histogram), Au/polycrystalline-NiNb annealed at 400 °C (middle histogram), and Au/a-NiNb annealed at 550 °C (bottom histogram). The vertical dotted lines indicate scattering from atoms at the surface (S and I).

number of Ni atoms, but rather by the density change which results in the near interface region when the Nb and Au interdiffuse. Au/a-NiNb samples were annealed isothermally at 490, 525, 550, and 600 °C. In addition, one sample of Au/polycrystalline NiNb was annealed at 400 °C. Although not measured, the crystallite size of this polycrystalline sample is expected to be approximately equal to the film thickness ($\sim 1 \mu\text{m}$).

III. ANALYSIS AND DISCUSSION

Analysis of the backscattering data was accomplished using a numerical code to compute the concentration as a function of depth for each element in the sample. The code involved an iteration process whereby the stopping power of the target was calculated using the depth concentration profile resulting from the previous cycle. This scheme always converged within three or four passes. The use of stopping powers, which varied in depth according to the beam energy and the atomic makeup of the sample, was necessary for an accurate interpretation of not only the depth scales but also the concentrations.

An example of such an analysis is shown in Fig. 2, where the Au and Nb atomic fractions are plotted versus depth for amorphous samples annealed at 550 °C for 0.25, 1, and 3 h. As mentioned above, the Ni profile did not vary appreciably and is therefore not plotted here. It should be noted however that, although small, the changes in the Ni profile do have a maximum effect of $\sim 5\%$ on the near-sur-

face concentrations of the other two elements. This figure shows that, even for the shortest anneal of 0.25 h, a significant amount of Au and Nb interdiffuse ($\sim 10\%$). In fact, a pronounced enhancement of the atomic movement was observed at all temperatures for the first 0.25-h anneal, which was followed by a slower interdiffusion for longer times. This initial rapid motion is probably due to the structural relaxation which metallic glasses are known to undergo.⁶ Further study of structural relaxation effects in deposited amorphous films is in progress, but it appears that a relaxed film may provide a more effective diffusion barrier than an unrelaxed film. For the longer anneals of 1 and 3 h, Fig. 2 shows the advancement of a 20 at. % Au plateau into the NiNb at the expense of Au atoms in the overlayer. A corresponding $\sim 20\%$ reduction in the Nb is also observed, indicating that the composition of this near-interface region becomes $\sim \text{Ni}_{0.5}\text{Nb}_{0.3}\text{Au}_{0.2}$. This apparent $\sim 20\%$ solubility for Au was also observed at 525 and 600 °C, whereas at 490 °C it dropped to only 5%. It is interesting to note that the

FIG. 2. Au and Nb concentrations vs depth for three anneal times at 550 °C for Au/a-NiNb. The Ni profile changes little for these anneals and therefore has not been plotted.

20% Au concentration observed above 500 °C corresponds to an Au/Nb ratio of 2/3, which is similar to the composition of the Au_2Nb_3 compound reported by Röschel *et al.*¹¹

The polycrystalline NiNb film did not exhibit a solubility limit for Au when annealed at 400 °C. The fact that a significant amount of Au motion into the polycrystalline NiNb was observed at a temperature of only 400 °C, with no indication of an upper bound on solubility, indicates that such a metallization would be much inferior to one made from α -NiNb on the basis of Au interdiffusion.

In order to calculate the diffusion coefficient of Au into α -NiNb, we assume that the atomic transport is described by the Doremus model for interdiffusion.¹² A more complicated analysis was deemed unsuitable due to the limitations of the data. It was also found that important parameters, such as diffusion lengths, were not terribly sensitive to the analysis used. In this model Fick's Law is solved with a concentration-dependent diffusion coefficient D , which is defined by

$$\frac{1}{D} = \left(\frac{C(x)}{C_0} \right) \frac{1}{D_{\text{Nb}}} + \left(1 - \frac{C(x)}{C_0} \right) \frac{1}{D_{\text{Au}}}, \quad (1)$$

where D_{Au} and D_{Nb} are the diffusion coefficient for Au and Nb, respectively, and $C(x)$ and C_0 are the Au concentration at depth x from the interface and at saturation, respectively. Lanford *et al.*¹³ have recently solved the diffusion equation, using this form for the diffusion coefficient, to obtain the equation

$$\frac{\partial^2 c}{\partial y^2} = -2y(1+bc) \frac{\partial c}{\partial y} + \left[b \left(\frac{\partial c}{\partial y} \right)^2 \right] / (1+bc), \quad (2)$$

where $c \equiv C/C_0$, $y \equiv x/(4D_{\text{Au}}t)^{1/2}$ and $b \equiv (D_{\text{Au}}/D_{\text{Nb}}) - 1$. This differential equation was solved numerically as a function of b , and we have reproduced some of our results in Fig. 3, where C/C_0 is plotted versus $x/x_{1/2}$ ($x_{1/2}$ is the depth

FIG. 3. Normalized Au profiles resulting from the Doremus model calculations for $D_{\text{Nb}}/D_{\text{Au}} = 1$ (dashed), 100 (solid), and 10 000 (dot-dashed); the data (squares) shown are for a Au/a-NiNb sample annealed at 550 °C for 2 h.

FIG. 4. Normalized Au profiles for Au/a-NiNb samples annealed at the indicated temperature. The solid curve results from the Doremus model calculation for $D_{\text{Nb}}/D_{\text{Au}} = 100$.

where $C/C_0 = 1/2$) for $D_{\text{Nb}}/D_{\text{Au}}$ ratios of 1, 100, and 10 000. Also plotted in this figure is the normalized Au profile data measured after a 2-h, 550-°C anneal. A good fit is obtained for $D_{\text{Nb}}/D_{\text{Au}} = 100$.

In Fig. 4 we have plotted selected Au profiles for each temperature along with the profile predicted by the Doremus mode for $D_{\text{Nb}}/D_{\text{Au}} = 100$. The agreement is reasonably good at all temperatures indicating that, over this narrow temperature range (490–600 °C), $D_{\text{Nb}}/D_{\text{Au}} \approx 100$. For this condition, the calculations by Lanford¹³ can be reduced to show that

FIG. 5. The characteristic extent of Au diffusion ($x_{1/2}$) from the Au/a-NiNb interface as a function of $\sqrt{t}$ for anneals at 490, 525, 550, and 600 °C. See text for details.

FIG. 6. Least-square fits of Eq. (4) to Au profiles of Au/polycrystalline NiNb samples before (solid line = theory; solid squares = data) and after (dashed line = theory; open squares = data) a 400 °C anneal for 30 min.

$$x_{1/2} = 2.92 (D_{Au} t)^{1/2}. \quad (3)$$

Equation (3) indicates that plotting $x_{1/2}$ versus $\sqrt{t}$ should yield a straight line with a slope of $2.92 \sqrt{D}$. Such a plot is given in Fig. 5 for the four anneal temperatures used in this investigation. The data do exhibit a linear behavior, and the solid lines in this figure result from error-weighted least-squares fits of the data to Eq. (3).

The Doremus model is not applicable in the case of Au diffusion in polycrystalline NiNb because, for this system,

the primary atomic transport mechanism is grain boundary (GB) diffusion. To extract a diffusion coefficient from these data, we utilize the theoretical results of Gupta *et al.*¹⁴ for the case of C-kinetics (i.e., the GB diffusion coefficient is far greater than the lattice diffusion coefficient). Under this approximation, the Au profile takes on a form involving error functions

$$\frac{C}{C_0} = 0.5 \left[\operatorname{erf} \left(\frac{a-x}{2(\Delta^2 + Dt)^{1/2}} \right) + \operatorname{erf} \left(\frac{a+x}{2(\Delta^2 + Dt)^{1/2}} \right) \right], \quad (4)$$

where a is the Au film thickness, x is the depth measured from the surface, and Δ is the depth resolution. This function has been fit to Au profiles taken for Au/polycrystalline NiNb samples before and after a 400 °C 30-min anneal. The data and fits are shown in Fig. 6. The parameters providing the best fits were $a = 195 \text{ Å}$, $\Delta = 29 \text{ Å}$, and $D_{Au} = 1.6 \times 10^{-15} \text{ cm}^2/\text{s}$.

The diffusion coefficients extracted from the data in Fig. 5 are given in the form of an Arrhenius plot in Fig. 7. The D_{Au} measured for the polycrystalline NiNb film is also indicated in this figure together with the extrapolated diffusion coefficient for Au in single-crystal Ni¹⁵ (c-Ni) for reference. The solid line in Fig. 7 results from a least-square fit of the a -NiNb diffusion coefficients to the equation

$$D = D_0 e^{-E_a/kT}, \quad (5)$$

where D_0 is the pre-exponential factor and E_a is the diffusion activation enthalpy. E_a was found to be 3.7 eV. Also indicated in Fig. 7 is a scale indicating the diffusion length $x_{1/2}$, for a period of one year for Au in a a -NiNb. For the polycrystalline NiNb and the c-Ni, the $x_{1/2}$ scale should be multiplied by $1/(2.92)^2$ to account for the different rates of Au transport described by Eqs. (2) and (4).

From Fig. 7 it is clear that Au undergoes significantly less diffusion in a a -NiNb than in polycrystalline NiNb. For

FIG. 7. An Arrhenius plot of the diffusion coefficient D for Au in amorphous and polycrystalline NiNb. The right-hand scale shows the diffusion length for a period of one year.

example, at 400 °C, D for Au in polycrystalline NiNb is > 6 orders of magnitude greater than the extrapolated D to Au in α -NiNb. While this extrapolation is based upon the use of Eq. (5) to describe the T dependence of D (which has not been established for amorphous alloys over wide T range) and the assumption of no crystallization over long times (10^4 h), it is clear that the measured D for α -NiNb at 490 °C is about 10^{-3} D (polycrystalline) at 400 °C. From this basis, the results indicate that if Au interdiffusion were the primary failure mechanism for contacts operated under identical conditions, an α -NiNb contact would survive > 1000 times longer at 400 °C than would a polycrystalline NiNb contact.

IV. SUMMARY

Interdiffusion between thin Au overlayers and amorphous and polycrystalline NiNb films have been measured following isochronal annealing by RBS analysis. The calculated diffusion coefficient D for Au in polycrystalline NiNb at 400 °C is 1.6×10^{-15} cm²/s, which is $> 10^6$ times greater than the extrapolated D for Au in α -NiNb at the same temperature. This result supports in the view that amorphous metal films will provide superior solid-state device metallizations for high-temperature applications.

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