PHYSICAL REVIEW B VOLUME 32, NUMBER 5 1 SEPTEMBER 1985

Crucial role of residual gases in amorphization of crystalline films

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(Received 20 December 1984)

A series of recent studies has claimed the amorphization of a crystalline multilayer film by a solid-state reaction during a vacuum anneal. The present study on Ni-Zr alloys establishes in two ways that the residual gases present in a vacuum system [$(4-6\times10^{-7}$ Torr] play an important role in the amorphization process. First, the superconducting transition temperature (which is sensitive to such residual gases) of as-deposited amorphous Ni-Zr films decreases and eventually vanishes during annealing treatments similar to those used in the amorphization of multilayers. The amorphized multilayers are superconducting at much lower temperatures than amorphous films of similar compositions. Second, annealing the multilayers in such a way as to avoid the effect of residual gases (*in situ* annealing in a protective getter-sputtering atmosphere) does not lead to amorphization.

I. INTRODUCTION

A series of recent studies[1-5] has claimed the amorphization of crystalline multilayer films by a solid-state reaction occurring during a vacuum anneal. The solid-state diffusion is thought to occur when one of the elements of the binary system [e.g., Au in La (Ref. 1), Ni in Zr (Refs. 3 and 4) and in Hf (Ref. 5)] exhibits an anomalous fast diffusion which was demonstrated by backscattering spectrometry. However, all these binary systems have in common an element (Y, Zr, Hf, and La) which is known to getter oxygen very efficiently. Indeed, the possibility of oxygen contamination was raised twice by the authors of the amorphization studies: The concentration of oxygen was found to increase after annealing Ni-Zr layers in a rough vacuum,[4] while Van Rossum *et al.*[5] suggested that the film surface is contaminated with oxygen after removal from the evaporation chamber and reported, using x-ray diffraction, occasional traces of HfO_2 after reaction but not in as-deposited films. This raises the important question of whether the amorphization is not the result of oxygen diffusing along with the fast-diffusing element (e.g., Ni) and, therefore, whether the resulting amorphous films are not different from both amorphous films obtained by vapor deposition and melt-spun glasses as a result of oxygen incorporation.

On the other hand, it has been well established that the superconducting transition temperature (T_c) of transition-metal elements[6-8] such as Nb and Ta and of rare-earth elements such as La (Ref. 9) is extremely sensitive to small amounts of oxygen undetectable by x-ray diffraction. Since amorphous Ni-Zr alloys are superconducting,[10] T_c will be used as a measure of the purity of amorphous films prepared by vapor deposition and by diffusion in multilayers and as a probe of the effects of vacuum annealing. Furthermore, since getter-sputtering is a technique which provides a concentration of reactive gases[6,8] (H_2O, O_2, and N_2) comparable to that of an ultrahigh vacuum (10^{-12} Torr), it will be used in the annealing of the multilayers and compared with the standard vacuum anneal.[3,5]

II. EXPERIMENTAL PROCEDURE

All the amorphous films of the present study ($Ni_{20}Zr_{80}$ and $Ni_{45}Zr_{55}$) were deposited by the getter-sputtering technique[6,8] at a power of 30 W (2000 V, 15 mA) onto sapphire substrates. The substrates were located on a tantalum heater table which was heated resistively to achieve deposition temperatures (T_D) above room temperature. The multilayer films consisted of alternate deposition by getter-sputtering of ten 300-Å-thick Ni layers and ten 780-Å-thick Zr layers. This corresponds to an average composition of $Ni_{45}Zr_{55}$. The sputtering power for the multilayers was kept at 6 W (1500 V, 4 mA) so as to keep T_D close to room temperature. The multilayer films were annealed in two different ways: as in most previous studies[3,5] the films were taken out of the deposition apparatus and annealed in a vacuum of $4-6\times10^{-7}$ Torr; alternatively, the multilayers were annealed *in situ* by covering the deposited film with a shield and sputtering Zr at 6 W while heating the multilayers for the desired length of time. The superconducting T_c were determined resistively for $T_c > 1.00$ K and inductively for $T_c < 1.00$ K.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Sputtered amorphous Ni-Zr films

The two compositions studied were chosen for the following reasons: $Ni_{20}Zr_{80}$ because it has the highest T_c of the Ni-Zr amorphous alloys[10] and $Ni_{45}Zr_{55}$ because this composition lies in the range where one can expect a single-phase amorphous product[3,5] after annealing the multilayers. The T_c and room-temperature resistivity ρ are listed in Table I as a function of T_D and film thickness (t). The main result shown in Table I is that T_c in-

TABLE I. Properties of Ni-Zr amorphous films.

Sample	T_D (K)	t (μm)	$\rho_{300\,K}$ ($\mu\Omega$ cm)	T_c (K)
$Ni_{20}Zr_{80}$ no. 1	77	0.44	955	<0.98
$Ni_{20}Zr_{80}$ no. 2	260	2.27	605	2.64
$Ni_{20}Zr_{80}$ no. 3	413	2.38	309	3.21
$Ni_{20}Zr_{80}$ no. 4	473	0.26	563	1.09
$Ni_{20}Zr_{80}$ no. 5	508	0.67	294	1.92
$Ni_{20}Zr_{80}$ no. 6	508	1.99	180	3.32
$Ni_{20}Zr_{80}$ no. 7	508	3.39	153	3.38
$Ni_{20}Zr_{80}$ no. 8[a]	593	0.80	120	2.76
$Ni_{20}Zr_{80}$ glass[b]		20	160	3.97
$Ni_{45}Zr_{55}$ no. 1	508	1.89	443	<1.00
$Ni_{45}Zr_{55}$ no. 2	593	3.42	459	1.26
$Ni_{45}Zr_{55}$ no. 3	693	3.48	313	1.37
$Ni_{45}Zr_{55}$ no. 4[a]	793	3.21	180	1.55
$Ni_{45}Zr_{55}$ glass[b]		20	185	1.83

[a]Partially crystalline.
[b]From Ref. 10.

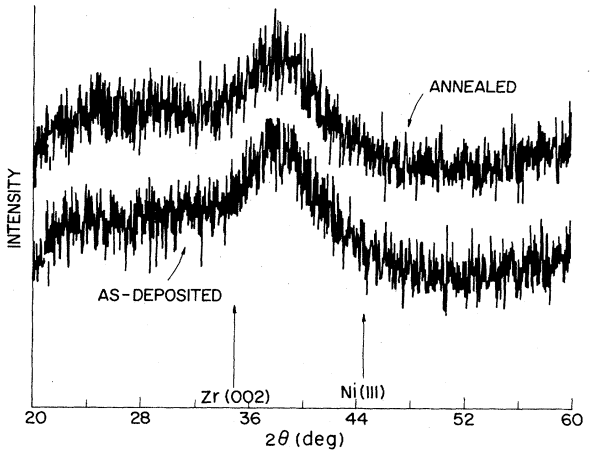

FIG. 1. X-ray diffractometer patterns for $Ni_{45}Zr_{55}$ no. 2: bottom, film in the as-deposited state ($T_D=593$ K); top, film annealed 17 h at 593 K *in vacuo* of $(4-6)\times10^{-7}$ Torr. The intensity (300 counts full scale) is the same for both patterns.

creases with increasing T_D and t. This result is even true if T_D is high enough to cause incipient crystallization as shown by comparison of $Ni_{20}Zr_{80}$ nos. 5 and 8 and of $Ni_{45}Zr_{55}$ nos. 3 and 4. The higher crystallization temperature for $Ni_{45}Zr_{55}$ of 793 K versus 593 K for $Ni_{20}Zr_{80}$ is consistent with the idea that the most stable amorphous alloy should be nearly equiatomic. It is also clear from Table I that for both compositions, both T_c and ρ for the thickest films sputtered at the highest T_D approach the corresponding parameters of the melt-spun glasses. This is consistent with the idea that a high T_D (short of crystallization) and a high t (which is equivalent to longer annealing times at T_D of the already deposited material) tend to promote a less distorted structure closer to an equilibrium glass. Having established the properties of as-deposited amorphous Ni-Zr films, the study will now proceed by investigating how these properties are affected by the type of annealing treatment used in the solid-state reaction of multilayers.

Typically,[3,5] the film thickness of the multilayer samples is below 1 μm, the annealing times ranged from several hours up to a week, and the annealing temperature is 573 K. Although ideally one would like to use similar conditions for the annealing of amorphous films, it is not always possible because, for example, the T_c of $Ni_{45}Zr_{55}$ films thinner than 1 μm is too low. Nevertheless, the effect of annealing in a $(4-6)\times10^{-7}$-Torr vacuum (which is as good as the best reported[5] vacuum for the multilayer anneal) is well demonstrated by the anneal of $Ni_{20}Zr_{80}$ no. 5. Indeed, as shown in Table II, a 21-h anneal of that 6700-Å film at 593 K lowers T_c from 1.92 K to below 1.00 K. A similar effect is shown by the anneal of $Ni_{45}Zr_{55}$ no. 2; although the measured drop in T_c is less, it is nevertheless impressive considering the fact that the film is 3.42 μm thick. One should also notice that although T_c is very sensitive to these annealing treatments, both the room-temperature resistivity (or the resistivity at 4.2 K which is only a few percent higher) and the amorphous diffraction pattern shown in Fig. 1 remain essentially unchanged. The decrease in T_c with annealing time depends, of course, on film thickness, as shown by the annealing data of $Ni_{20}Zr_{80}$ nos. 5 and 7 (Table II). A further complication arises when the annealing temperature is below T_D: annealing at 593 K, $Ni_{45}Zr_{55}$ no. 3, which was deposited at 693 K, leaves T_c unchanged but longer annealing times at T_D or even below T_D as for $Ni_{45}Zr_{55}$ no. 4 eventually depresses T_c below 1.00 K. Finally, a particularly striking example of the deleterious effects of vacuum anneals is shown by comparing the 8000-Å $Ni_{20}Zr_{80}$ no. 8 film deposited at 593 K with a T_c of 2.76 K (Table I) with the much thicker 3.39-μm $Ni_{20}Zr_{80}$ no. 7 film which only had a T_c of 1.08 K (Table II) after a week of annealing at the same temperature of 593 K. It is therefore clear from all the experiments described in Table II that the same types of annealing treatments used to interdiffuse multilayers contaminate the amorphous films. One can furthermore expect the contamination to be worse in the multilayer experiments because in this case one has a fast-diffusing element (Ni) which can provide fast-diffusion paths for the residual gases (oxygen, in particular), while amorphous films are essentially stable structures where annealing only causes adatomic motions for lattice relaxation. One should also point out that contamination in a vacuum system even during deposition has been known for a very long time and, quoting from Holland,[11] "such contamination can arise from the gas molecules impinging on the substrate during deposition, and this source of contamination has often been ignored . . . ." Indeed, in a vacuum of 5×10^{-7} Torr the ratio of metal atoms to impinging gas molecules is about 25 to 1 assuming a deposition rate of 10 Å/sec. It is therefore not surprising that exposing the small amount of material of a film to such an impingement rate for a long time will contaminate the film.

TABLE II. Vacuum anneal of Ni-Zr films.

Sample	Annealing treatment	$\rho_{300\,K}$ ($\mu\Omega$ cm)	T_c (K)
$Ni_{20}Zr_{80}$ no. 5	as-deposited at 508 K	294	1.92
	21 h at 593 K	294	<1.00
$Ni_{20}Zr_{80}$ no. 7	as-deposited at 508 K	153	3.38
	90 h at 593 K	160	1.89
	+66 h at 593 K[a]	140	1.08
$Ni_{45}Zr_{55}$ no. 2	as-deposited at 593 K	459	1.26
	17 h at 593 K	463	<1.00
$Ni_{45}Zr_{55}$ no. 3	as-deposited at 693 K	313	1.37
	17 h at 593 K	313	1.37
	+71 h at 693 K[a]	260	<0.98
$Ni_{45}Zr_{55}$ no. 4	as-deposited at 793 K[a]	180	1.55
	71 h at 693 K[a]	160	<0.98
$Ni_{45}Zr_{55}$ no. 5 multilayer film	21 h at 593 K	161	0.58–0.76
$Ni_{45}Zr_{55}$ no. 6 multilayer film	21 h at 593 K *in situ*	41	0.60–0.80

[a]Partially Crystalline

B. Multilayer $Ni_{45}Zr_{55}$ films

A multilayer film consisting of ten 300-Å-thick Ni layers alternating with ten 780-Å-thick Zr layers (which corresponds to a nominal composition of $Ni_{45}Zr_{55}$) was deposited at 320 K and the corresponding x-ray diffraction pattern is shown as the upper trace of Fig. 2. This

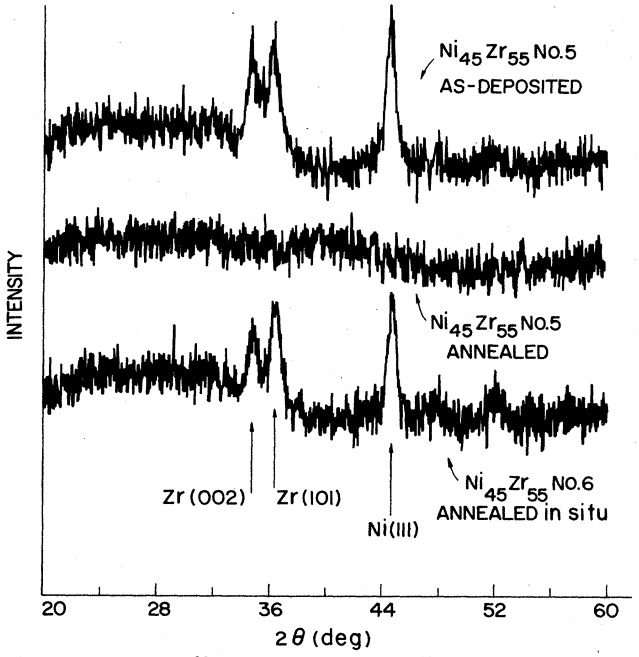

FIG. 2. X-ray diffractometer patterns for multilayer films: top, $Ni_{45}Zr_{55}$ no. 5 as-deposited at $T_D=320$ K; middle, $Ni_{45}Zr_{55}$ no. 5 annealed for 21 h at 593 K *in vacuo* of $(4-6)\times10^{-7}$ Torr; bottom, $Ni_{45}Zr_{55}$ no. 6 annealed *in situ* under getter-sputtering atmosphere at 593 K for 21 h. The intensity scale is the same for all patterns.

film was taken out of the deposition apparatus before annealing in a vacuum of $(4-6)\times10^{-7}$ Torr for 21 h at 593 K, and in agreement with previous studies the crystalline layers have been amorphized by the heat treatment (Fig. 2, middle trace). The diffraction pattern for this amorphized multilayer is, however, much more diffuse than the amorphous pattern shown in Fig. 1 for an as-deposited $Ni_{45}Zr_{55}$ film. This difference may arise from the fact that amorphized multilayers are characterized by a broad compositional range:[5] an original 60-at. % Ni-Hf multilayer displayed after diffusion a range of 45–70 at. % Ni. Furthermore, similar to heat-treated amorphous Ni-Zr films, this amorphized layer has a very low T_c (0.58–0.76 K), one barely higher than that of bulk Zr (0.61 ± 0.15 K). This is particularly bad since in analogy with the Ni-Hf multilayers such a film most probably contains regions with much higher Zr content ($\simeq$70 at. %) which should be superconducting above 3 K.[10]

In order to minimize as much as possible the contamination by oxygen, a multilayer film will now be annealed *in situ*. Although an *in situ* annealing treatment has been used once before,[2] as discussed above, it still does not avoid the contamination effects caused by the high impingement rate of the residual gases present in a 10^{-7} Torr vacuum. For this reason, the annealing of the multilayer was performed *in situ* while getter-sputtering Zr onto a shield which prevents further deposition on the multilayer. It has been previously established[5,8] that this procedure provides a concentration of reactive gases (O_2, in particular) comparable to that of an ultrahigh vacuum (10^{-12} Torr). The result of this heat treatment is shown as the bottom diffraction pattern of Fig. 2 and it is clear that except for a slight reduction in intensity of the crystalline diffraction peaks (by comparison with the top diffraction pattern) the film is still crystalline. Consequently, comparing conventionally annealed $Ni_{45}Zr_{55}$ no. 5 with

the getter-sputtering atmosphere anneal of $Ni_{45}Zr_{55}$ no. 6, both performed for 21 h at 593 K and both 1.08 μm thick, it is clear that the latter multilayer film was not amorphized. Furthermore, as shown in Table II, sample no. 6 has a much lower resistivity than sample no. 5 and the somewhat higher T_c than in bulk Zr could reflect a partial amorphization of the film. Conversely, the same T_c displayed by sample no. 5 reflects some remaining crystalline portions in the film.

IV. SUMMARY

Although vacuum annealing of crystalline multilayers undoubtedly results in amorphous films, such films are different from both vapor-deposited films and glasses: they do not possess a sharp composition and are contaminated by residual gases. The contamination was demonstrated by the depression of T_c as a result of conventional vacuum annealing and by the absence of amorphization when annealing under a getter-sputtering atmosphere which has a very low concentration ($\approx 10^{-12}$) of reactive gases.

ACKNOWLEDGMENTS

I would like to thank G. W. Hull of Bell Communications Research, Inc. (Murray Hill, NJ) for the low-temperature superconductivity measurements, and R. J. Felder for his able technical assistance.

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