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INTERFACE CONTROLLED AMORPHIZATION OF CRYSTALLINE Ni/Ti MULTILAYERS

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ABSTRACT

Solid-State Amorphization (SSA) of crystalline interfaces is observed in the Ni/Ti multilayer system. The amorphization reaction nucleates at location(s) of crystallographic disorder, i.e. the multilayer interfaces. Microstructural analyses reveal the sputter-deposited growth structure to be epitaxial with semi-coherent interfaces. Strain energy originating from interface lattice distortions varies as a function of the multilayer repeat spacing. Therefore, the interfacial energy effects the onset conditions for SSA. Differential thermal analysis is used to measure the critical temperature T_c, to the nucleation of the SSA, which is found to vary with the Ni/Ti multilayer pair spacing.

INTRODUCTION

Solid-state amorphization (SSA) is the crystalline to amorphous phase transformation.[1] The assessment of experimental observations of SSA are often complicated by complex process conditions. In ball-milled samples, large plastic strains are generated from the external loading process.[2] In conventional theoretical assessments, SSA is modelled as the interdiffusion process between an ordered and amorphous phase.[3] If the amorphization reaction progresses without an amorphous parent phase, however, then it is first necessary to have a classic nucleation of the amorphous phase. We propose that the nucleation of a disordered phase occurs at the locations in a crystalline system which have the greatest degree of disorder, i.e. internal interfaces. The use of crystalline multilayers addresses these issues. First, SSA nucleation will be at crystalline interfaces (i.e. no parent amorphous phase) and secondly, the SSA process will be initiated solely by thermal activation (removing the need for complex external loading conditions). A means to regulate the driving force of SSA nucleation is approached through a systematic variation of the crystalline interface spacing, i.e. the multilayer pair spacing. It is well established that lattice strains produced at the interfaces vary with the layer pair spacing. Therefore, interfacial strain effects the critical temperature T_c of SSA as a consequence of adding interfacial elastic energy to the chemical component of the energetic barrier to the crystalline-to-amorphous phase transformation.

The Ni/Ti multilayer system is ideal to study SSA since there is a large atomic size difference between the elements and a deep eutectic is found near 25 $^a/_o$Ni in the binary phase diagram. In prior studies of sputtered multilayers, microstructural characterization reveals the Ni/Ti interfaces to be amorphous.[4-6] For these multilayers, the energetics of the deposition process are sufficiently high enough to create an amorphous phase during the growth process as a consequence of ballistic adatom bombardment and intermixing. In this study, the sputter deposition parameters of working gas pressure, source-to-substrate separation and discharge voltage are selected to promote near thermalization of the sputtered neutrals, thereby minimizing adatom intermixing in the evolving film, to produce multilayers with crystalline interfaces.[7]

SAMPLE PREPARATION

The deposition chamber is cryogenically pumped to a $1.3\text{x}10^{-5}$ Pa base pressure. A circular array of planar magnetron sources is situated 20 cm beneath an oxygen-free copper platen. The sputter sources are operated in the dc mode at a 240-340 V discharge. An argon working gas pressure of 0.40 Pa is used at a 14-15 cc min^{-1} flow rate. Substrates are sequentially rotated over each source at 0.03-0.40 rev min^{-1} to produce N multilayer pairs. The target materials are >0.9994 pure. The Si(111) wafer and cleaved (muscovite) mica substrates are pre-cleaned with a detergent wash, deionized water rinse, alcohol rinse and a N_2 gas drying. The substrate temperature remains at 20-33 °C during deposition. Deposition rates of 0.1-0.2 nm sec^{-1} are monitored using quartz crystals. Crystal monitors record the individual layer thicknesses t_{Ni} and t_{Ti} which are used to compute the layer pair spacing $d_{Ni/Ti} = (t_{Ni}+t_{Ti})$, and $\Gamma_{Ni} = (t_{Ni} \div d_{Ni/Ti})$. The 0.3-0.4 μm thick multilayer films are floated from the mica substrates using deionized water and air dried at room temperature for use in the DTA experiments. The Ni/Ti multilayer dimensions are listed in Table 1.

CHARACTERIZATION METHODS AND RESULTS

Transmission electron microscopy (TEM) and high resolution imaging provide a direct examination of the multilayer film morphology and lattice structure. High resolution imaging of cross-sectioned, Ni/Ti multilayers has revealed the Ni-Ti and Ti-Ni interfaces to be crystalline.[7-9] High resolution image simulations and electron diffraction patterns show that the Ni/Ti structure is a face-centered-cubic superlattice.[9] Bright field images of cross-sectioned, Ni/Ti samples reveal alternate light (Ti) and dark (Ni) layering (in Figs. 1a-c). The layering is smooth and continuous normal to the growth direction. The sputtered films are typified by dense columnar growth with a <50 nm average grain size. The Ni and Ti thicknesses verify the Table 1 - crystal monitor values.

Atomic concentration profiles are generated using Auger electron spectroscopy (AES) coupled with depth profiling. A 3 keV, 10 μA electron beam is used to generate the Auger electrons. The intensities of the 418 eV Ti^2 LMM, the 503 eV O^1 KLL and the 848 eV Ni^1 LMM peaks (from data accumulated in the derivative mode) are used to compute atomic concentrations. A 5 keV, 1.27 μA argon ion beam is used to etch a 25 mm^2 area of the film surface. The gas pressure for the sputter etch is $2\text{x}10^{-3}$ Pa whereas the Auger system base pressure is $6.7\text{x}10^{-8}$ Pa. Once the surface oxide is sputtered through, the film composition is found to be free of any contamination (Figs. 1d-f). The composition oscillations in the concentration profiles correspond to the multilayer pair spacing.

Table I. Ni/Ti Multilayer Parameters

$d_{Ni/Ti}$ (nm)	N	t_{Ni} (nm)	Γ_{Ni}	Γ_{AES}	W (mg)	T_c (°C)
3.0	118	0.93	0.31	0.35	1.95	410
7.0	61	1.68	0.24	0.28	1.50	414
14.0	21	3.64	0.26	0.26	1.50	361
20.2	15	5.86	0.29	0.28	2.20	340
26.3	9	5.79	0.22	0.24	1.40	307
35.4	12	13.5	0.38	0.35	3.30	315

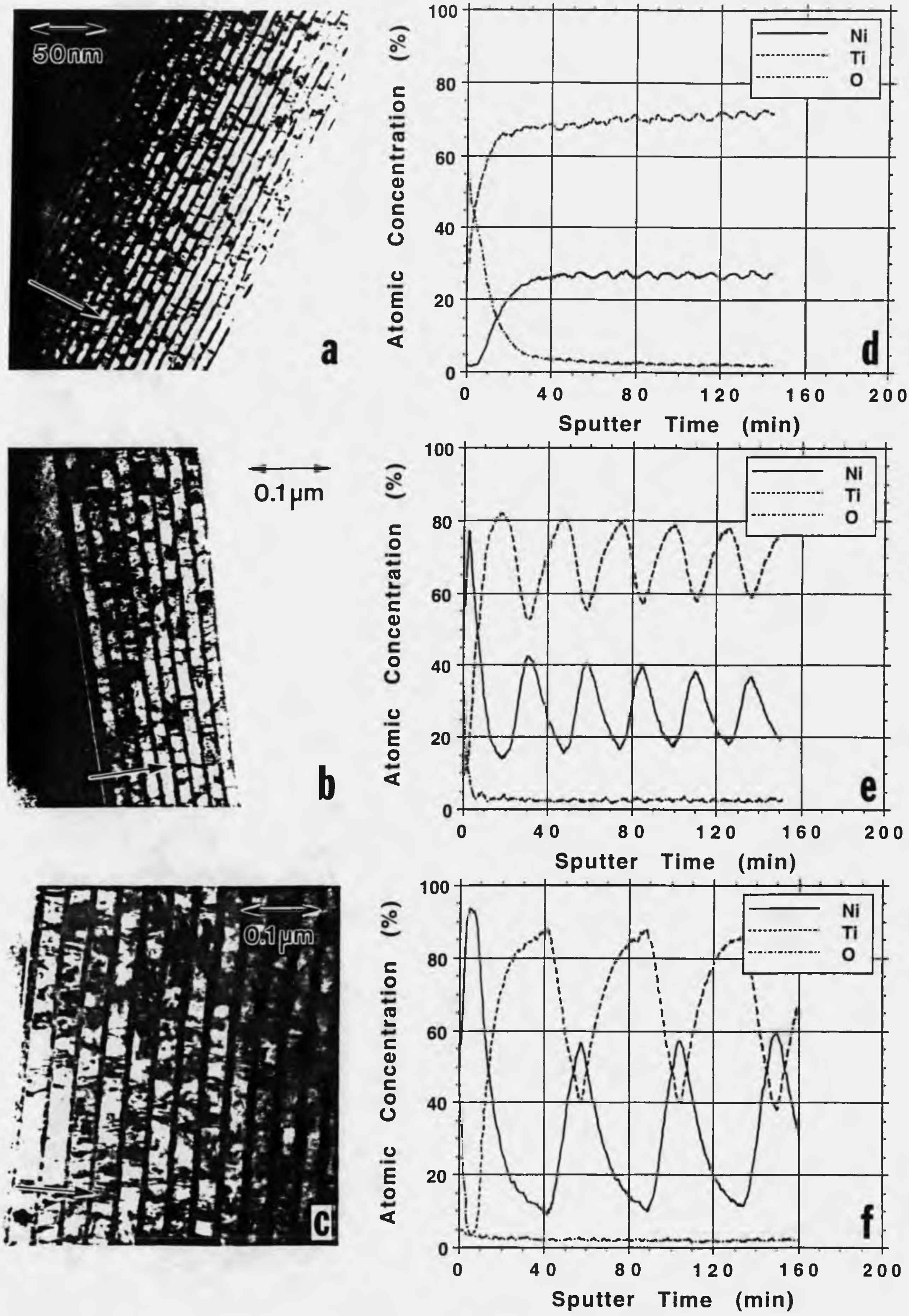
The average Ni profile concentration is measured as Γ_{AES} and listed in Table 1. The Γ_{AES} values are within 10% of the absolute values of Γ_{Ni}.

Differential thermal analysis (DTA) measures the difference in temperature ΔT between the multilayer sample and a standard as a function of increasing temperature. The standard (in this case an alumina powder) is selected using the criteria that it won't undergo a phase transformation in the temperature range of interest. Conventionally, endotherms denoted by a discontinuous decrease in temperature (at the critical transition T_c) signify melting, i.e. an increase in entropy. A crystalline-to-amorphous transformation statisfies the criteria of an increase in structural disorder. Analytically, an endotherm in the temperature trace of ΔT is where a negative change in slope is found, i.e. $\partial^2(\Delta T)/\partial T^2 < 0$, indicating SSA of the crystalline Ni/Ti multilayer structure. The Ni/Ti foils (cut to weights W listed in Table 1) are initially heated to 200 °C at a rate of 20 °C $\min^{-1}$, then slowly heated to 450 °C at a rate of 0.5 °C $\min^{-1}$. The DTA traces (Figs. 1g-i) reveal that a critical transition is found for each Ni/Ti sample. The multilayer pair spacing affects a change in the T_c of SSA (listed in Table 1). We find that heating rates <2.0 °C $\min^{-1}$ do not affect the location of T_c.

DISCUSSION & SUMMARY

Nucleation of SSA in a 26nm Ni/Ti multilayer is found at ~325 °C using in-situ TEM and high resolution lattice imaging.[8] This observation verifies the T_c of 307°C measured for the 26.3nm Ni/Ti (Table 1) validating the DTA assessment of the SSA transformation temperature. Analysis of x-ray diffraction scans reveals a square composition profile (with a computed interface roughness <0.5nm) composed of strained Ni (in tension) and Ti (in compression) layers.[10] All of the atomic planes in the superlattice are strained when $d_{Ni/Ti} < 10$ nm. The lattice strain relaxes from interface maxima to zero at the center of each layer when $d_{Ni/Ti} > 12$ nm. Loss of continuous strain, i.e. structural coherence, corresponds with a the decrease in T_c from ~410°C to ~310 °C.

The processes of SSA and thermodynamic melting are both shown to involve heterogeneous nucleation of disorder, with consideration of characteristic extended defects and high atomic mobility.[11,12] The T_c dependence of SSA upon the multilayer pair spacing $d_{Ni/Ti}$ can be analized in this context. At an elevated temperature, T_{oc}, the incoherent interface is energetically unfavorable compared to the amorphous (i.e. the liquid-like) state. Therefore nucleation of SSA


50nm
a
0.1μm
b
0.1μm
c
d
e
f
Atomic Concentration (%)
Sputter Time (min)
0
20
40
60
80
100
0
40
80
120
160
200
Ni
Ti
O

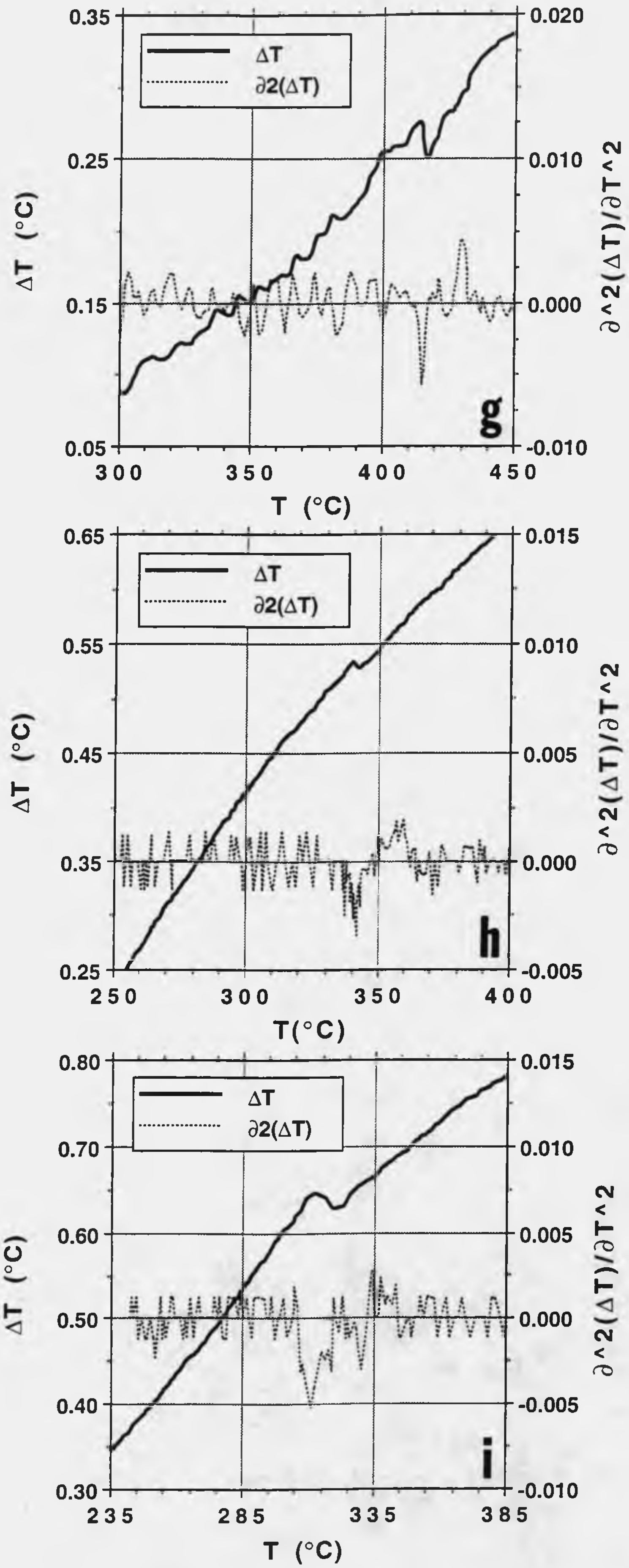


Figure 1. The Ni/Ti thin films are viewed in cross-section in these transmission electron microscope, bright field images of samples with multilayer pair spacings (nm) of (a) 7.0, (b) 20.2, and (c) 35.4. The layering is smooth and continuous normal to the film growth direction (as indicated with an arrow). Auger electron spectroscopy coupled with depth profiling is used to measure the Ni and Ti concentration variation through the samples with multilayer pair spacings (nm) of (d) 7.0, (e) 20.2, and (f) 35.4. The differential thermal analysis of the films reveals a phase transformation in each Ni/Ti sample with multilayer pair spacings of (g) 7.0, (h) 20.2, and (i) 35.4. An endotherm in the temperature trace of ΔT is confirmed by the negative change in slope, i.e. $\partial^2(\Delta T)/\partial T^2 < 0$. The endotherm indicates solid-state amorphization of the crystalline Ni/Ti multilayer structure.

occurs at T_{oc} for an incoherent superlattice. Onset of coherency with decreasing layer pair spacing lowers the interface entropy since the semi-coherent interfaces are less disordered than incoherent interfaces. The nucleation of SSA is thereby delayed to higher temperatures ($T_c > T_{oc}$) as the onset of coherency strains preserves structural order at the interface. A molecular dynamics model[13] of amorphization from Co/Zr multilayer interfaces describes SSA nucleation and the temperature dependence presently found in the Ni/Ti experimental results. Complete crystalline disorder (or amorphization) is described by the progressive decrease in the interface structure factor from 1 to 0 with increase in temperature. The simulation shows that interface amorphization develops while the layer bulk remains periodic. Upon further increase in temperature, the disorder spreads to the layer bulk, i.e. to the center of each layer. The temperature of disorder scales with the layer size.

In summary, SSA nucleates at sites of crystallographic disorder, namely the multilayer interfaces. Interfacial strain energy is attributed to lattice distortions which are dependent upon the multilayer pair spacing. The interfacial strain energy affects the critical temperature T_c of SSA which is measured using DTA. Our results detail the increase in T_c of amorphization as dependent on the loss of lattice coherency as a function of decreasing layer pair spacing in crystalline Ni/Ti multilayers. Our results agree with and supplement previous Ni/Ti findings.[4-8]

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