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RESEARCH ARTICLE

Effect of Sputtering Process Parameters on the Magnetron Sputtered Ni-Ti-Cu thin Films

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ABSTRACT

The shape memory effect, super-elasticity and biocompatibility allow the Ni-Ti-Cu thin films to be used in different fields. In this paper systematic study have been done on the Ni-Ti-Cu thin films with various copper content. The Ni-Ti-Cu films were successfully prepared by individual sputtering targets of pure Ti, Ni and Cu and the crystalline structure, residual stress and phase transformation properties of the Ni-Ti-Cu films were investigated using grazing incidence X-ray diffraction (GI-XRD), differential scanning calorimetery (DSC), and curvature measurement methods. The effects of the sputtering process parameters on the film composition, phase transformation and shape-memory effects were analyzed.

INTRODUCTION

Shape memory alloy (SMAs) have a suitable resistivity, which enables them to be actuated electrically by joule heating. When the current passes through the alloy, the heat generated is sufficient to cause the phase transformation. Compared to the bulk Ti-Ni alloys, the small thermal mass and large surface to volume ratios of Ti-Ni thin films reduce the time required for the device to cool down, allowing a faster heat transfer and an increase of the operation bandwidth. The applicability of binary Ti-Ni shape memory alloys (SMAs) for actuators is limited by their large thermal hysteresis and their comparatively low transformation temperatures (<100 ˚C) (Surbled, *et al*., 2001) while the width of the transformation hysteresis, of Ti-Ni based alloys can be reduced by alloying with Cu (Sanjabi *et al*., 2005). Also alloying with some other elements, such as for example, Au, Hf, Pd, Pt or Zr can result in a significant increase in transformation temperature (Humbeeck, 1997).Compared with the Ni-Ti binary alloy thin films, the ternary Ti-Ni-Cu alloys show less compositional sensitivity to martensite transformation temperature, a narrower temperature hysteresis and pseudoelasticity hysteresis, which makes them more suitable for microactuator material (Fu *et al*., 2003). In this investigation, Ti-Ni-Cu films were prepared by individual targets of the pure Ni, Ti and Cu (Zarnetta *et al*., 2011). In this study investigation of the effects of the processing parameters on the crystalline structure, phase transformation and shape memory effect of the Ti-Ni-Cu films were investigated and compared.

Experimental

Ti-Ni-Cu films were prepared by magnetron sputtering of individual Ti, Ni and Cu targets using RF and DC magnetron sputtering guns. The system includes four 3-inch planner high performance water-cooled magnetrons (with one 600 W RF generator and two 1 kW DC power supplies). The base pressure of main chamber was 3×10^{-6} mTorr. (1 0 0) type silicon wafers were used as the substrates. Thermo couples(tungsten carbide) were mounted to measure the deposition temperature. The substrate holder was rotated during the deposition to achieve the uniform deposition. The sputtering conditions were listed in Table 1. After the deposition, the films were annealed at 873 K to obtain the crystallization. The substrate-to-target distance was 125 mm. The argon pressure was changed from 30 to 10 mTorr. Film composition was determined by energy dispersive X-ray spectroscopy (EDS) using standard samples of pure Ti and Ni (purity, 99.99%). Surface and cross-section microstructures of thin films were studied by field emission scanning electron microscope (FESEM, ZEISS S5300). The martensitic transformation temperatures were measured by a Perkin Elmer DSC-7 at a heating/cooling rate of 5 K/min over a temperature range from 223 to 423 K. The crystalline structure of the films was determined by grazing incidence X-ray diffraction (Cu Ka 40 kV/30 mA) with different incident angles. The change of crystalline structure for the deposited films was analyzed by a Philips PW3719 X-ray diffraction (GIXRD) under different temperatures. The transmission electron microscopy have been used to correlate the GIXRD results. The curvature changes of film-deposited Si wafers were measured using a DEKTAK profilometry and the film stress values were measured using surface curvature methods and to check the shape memory property of the films low temperature resistivity have been done with Vander Pauw 4-probe electrical Measurement technique in CIP and CPP geometry.

RESULTS AND DISCUSSIONS

Microstructure and composition

In the Fig.1 shows high-temperature differential scanning calorimeter (DSC) result of the Ni-Ti-Cu films heating up to 573 K. The data clearly shows that the single peak on the heating curve corresponds to the martensite (monoclinic) to austenite (cubic) transformation, and

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as the concentration of the Cu increases in the Ni-Ti matrix the phase transformation temperature decreases (Fu *et al*., 2003).

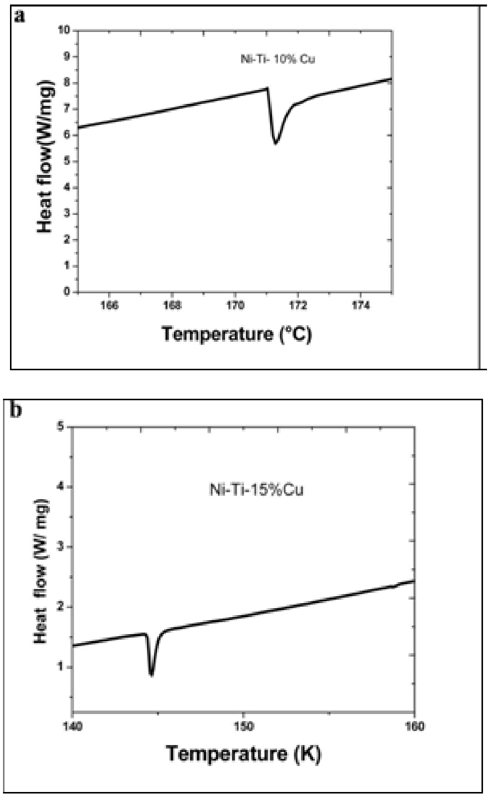


Figure 1: The DSC micrograph for the as deposited (a) Ni-Ti-10%Cu thin films and (b) Ni-Ti-15%Cu thin films

The Fig. 2(a)_(d) show FESEM image of planar and cross-sectional morphologies of the films deposited under different gas pressure, With a gas pressure of 30 mTorr, after depositing for 30min, the film surface shows coarse microstructure with some large cracks (Fig. 2(a)). Cross-section morphology shows in Fig. 2(b) the coarse columnar structure at 30 mTorr ,this type of columnar structure will cause brittleness of the films, and the film is easily broken together with the silicon substrate. When the Ar gas pressure decreased to 20 mTorr, the prepared films still have a column structure and there are many particles existed inside (Fig. 2(c)), whereas the film prepared under a low Ar gas pressure of 10 mTorr is very ductile and the film surface shows a smooth and featureless morphology. The cross-section morphology shows some tearing features and exhibits a uniform structure as shown in Fig. 2(d). For the as-deposited Ti-Ni-Cu film, after annealing at 873 K for 1 hr, the film is slightly densified compared to as-sputtered one, but the deposited columnar structure cannot be modified through the annealing process.

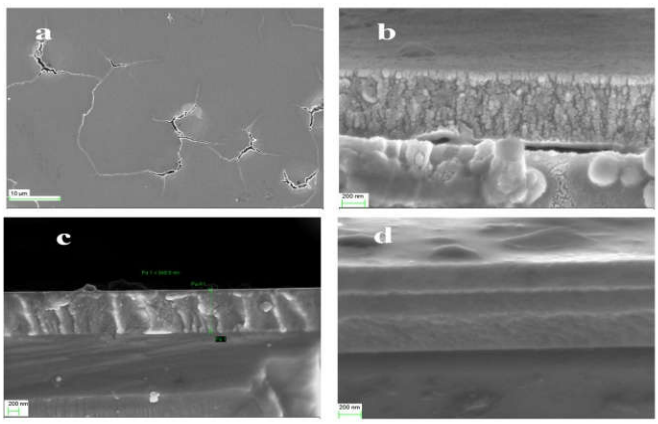


Figure 2: FESEM micrographs depicting the microstructure along the surface and the cross. sections of thin films of as-deposited Ti-Ni 10%Cu thin film (a) and (b) at 30 mTorr; (c) at 20 mTorr and (d) at 10 mTorr

The chemical composition of the sputtered thin films was changed with the variation of Cu target power, when fixing Ti and Ni target power of 250 W in RF and 71w in DC targets respectively. The determined chemical composition using EDX is listed in Table 1. The variation of measured composition on the whole wafer have been done and it shows that with an increase in the copper target power, the content of nickel decreases whereas copper content increases. The chemical composition of the sputtered thin films was changed with the variation of Cu target power, when fixing Ti and Ni target power.

Table 1. Deposition conditions and chemical compositions of Ni-Ti-Cu thin films

sample	Ti target power(W)	Ni target power(W)	Cu target power(W)	Substrate temperature(K)	Duration (mins)	Film composition % Ni	% Ti	%Cu
1	250	71	8	300 to 773	30	42	48	10
2	250	71	10	300 to 773	30	41	44	15

Effect of substrate temperature on film crystallinity

The GIXRD measurement results can clearly reveal the post-annealing effect on crystallization of as-deposited Ti-Ni-Cu films under different substrate temperatures shows in Fig. 3. For films deposited at substrate temperature 300 K to 773 K, a predominantly amorphous structure is observed up to around 473K, but after 473 K the film starts to shows the crystalline structure and the crystalline nature of the film increases as the substrate temperature increases.

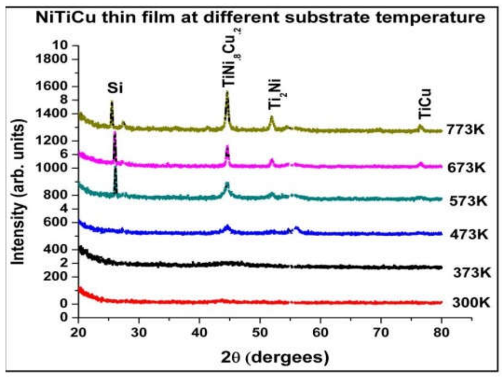


Figure 3: The GI-XRD plot for the as deposited Ni-Ti-10%Cu films at different substrate temperature

The crystalline structure is prominent when the substrate temperature is increased to 773K it can be observed in Fig. 3, where martensite is the major phase. The as-deposited Ti-Ni-Cu films showed featureless surfaces, which were smooth, shiny, and reflective. The GIXRD analysis indicated that these as-deposited films were mostly amorphous. To confirm the film crystallinity HRTEM image of the as-deposited film at 300K and 773K have been taken.

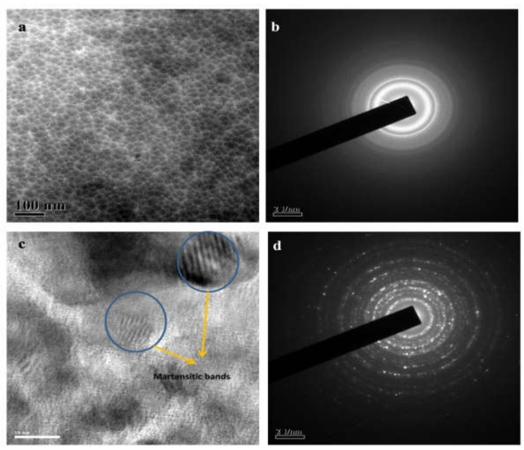


Figure 4: HRTEM micrographs of 600°C Ti-Ni-10%Cu film as-deposited and annealed (a),(c) bright field image and (b),(d) SAD pattern. Confirms the crystalline nature of the films

In the HRTEM image (Fig.4) of the as-deposited film shows the amorphous nature of the film deposited at 300K substrate temperature whereas, the HRTEM image of films deposited at 300K substrate temperature, shows the presence of nanocrystalline grains, associated with some martnsitic bands two the SAD patterns in Fig.4(b) and Fig.4(d) confirm the amorphous and nanocrystalline nature of the as-deposited and annealed films, respectively.

Effect of substrate temperature on grain size

FE-SEM observation, of the films deposited at different substrate temperature, after cooling to room temperature, revealed that clusters of circular grains had appeared on the film surface, surrounded by a featureless matrix shown in Fig.5 (Fu *et al*., 2006). In case of the surface topography shown in Fig.5 according to the structure zone model developed by Thornton (Thornton, 1974; Thornton, 1986) the substrate temperature influences the microstructure of sputtered thin films. The film microstructures were classified based on the T_s/T_m (T_s and T_m are the substrate temperature and the melting temperature of the deposited film, respectively) ratio and are categorized under four types of zones. When the substrate temperatures are such that the T_s/T_m ratio lies between 0 and 0.2, it represents the zone I type of film growth mechanism that supports the formation of amorphous films with a high density of trapped defects such as vacancies and interstitials. This structure belongs to a temperature range in which neither a bulk diffusion nor the self surface diffusion has remarkable effect. When T_s/T_m is between 0.2 and 0.4, it falls in zone T in which the surface diffusion is significant, whereas the grain boundary migration is strongly limited. Zone II is a consequence of the high surface mobility of the adatoms at high substrate temperatures resulting in grain boundaries that are nearly perpendicular to the film plane. Zone III is characterized by equiaxial three-dimensional grains because both surface and bulk diffusion of the adatoms takes place (Priyadarshini *et al*., 2011).These grains had diameters ranging from a few microns.

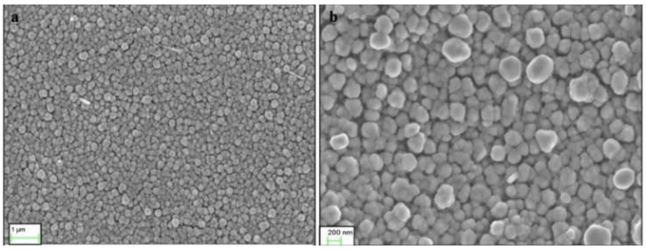
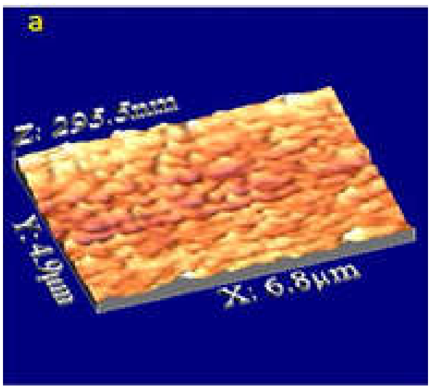
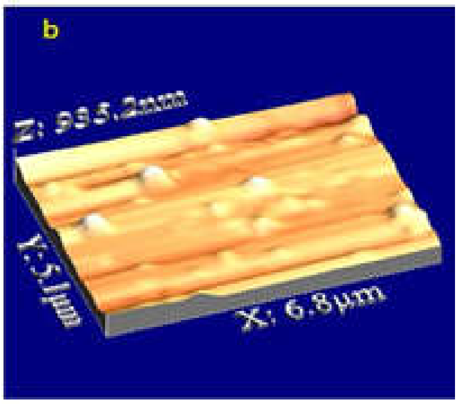


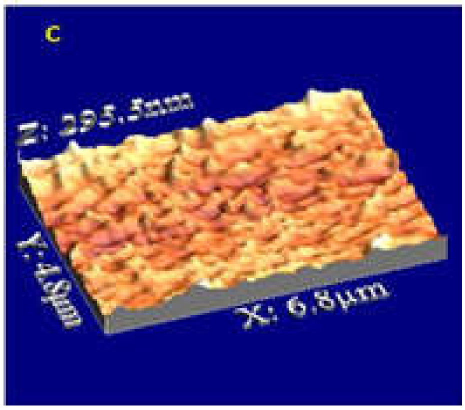
Figure 5: FESEM micrographs depicting the microstructure of thin films of as-deposited Ti-Ni 10%Cu films at different substrate temperature of (a) 573k (b) 773K

Effect of substrate bias on film thickness and roughness

A detailed study using AFM Fig.6 showed that the grains consist of inter weaving martensite structure, causing an surface relief morphology (Fu *et al*., 2006). From the Fig.7 it also shows the variation of the roughness of the film using the different bias condition it shows that as the bias voltage increases the roughness of the film decreases.







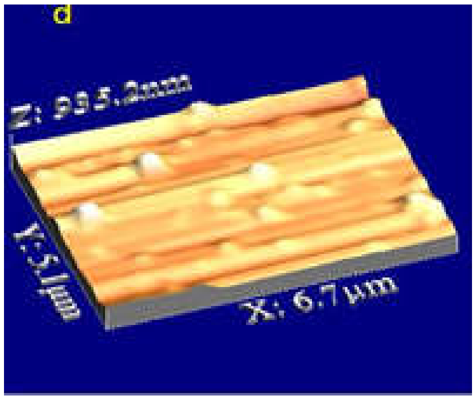
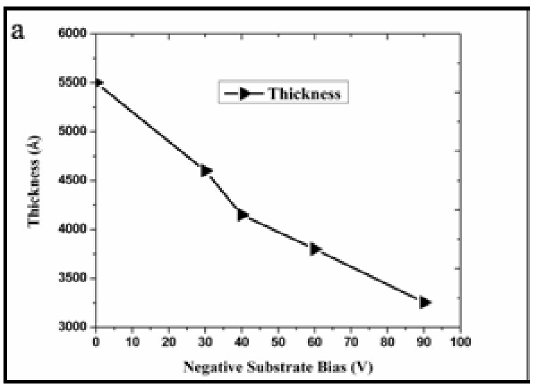


Figure 6: Variation of surface roughness AFM profile of Ti rich Ni-Ti-Cu films deposited at (a) and (c) 0V and (b) and (d) -60V for 10% and 15% Cu content respectively

The surface roughness in films grown at 0 V bias is due to the presence of large surface porosities. The occurrence of larger pores on the surface is due to (i) coalescence of voids at grain boundary or nano pores to reduce surface energy, as well as (ii) entrapment of argon gas in the films during deposition and subsequent escape from the surface (Mitra *et al*., 2001).



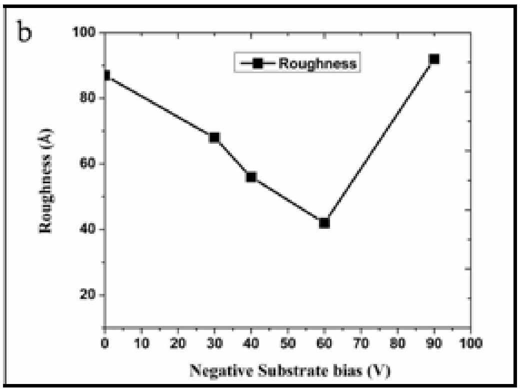


Figure 7: Variation of surface (a) thickness and (b) roughness profile Ni-Ti-10%Cu films deposited at different substrate bias

In Fig.7 the application of a moderate bias would reduce entrapment of argon because resputtering with argon ions would discourage sticking of neutral argon atoms to the films, which also decreases the film thickness at very high substrate bias.

Effect of substrate bias and substrate temperature on film residual stress and resistivity

The film residual stress calculation carried out with the help of the surface profilometry of stylus profilometer on the Ni-Ti-Cu thin films shown in Fig.9(a) indicate the change in average residual stress of the material with the applied substrate temperature. In Fig. 9(a) as the substrate temperature increases, the difference in temperature gradient between the substrate and deposited film decreases, which trend to decreases the average residual stress on the film surface. In Fig.7 (b) shows that as the substrate negative bias increases the film residual stress increases It may be due to the increase of the substrate bias, the adatome mobility increases which may cause increases of the island on the free surface of the substrate. In other word the nucleating island tend to be closer to one another and coalesce to reduce the net surface energy. It is also proposed from the literature (Mitra *et al*., 2001), the tensile stress are generated due to the interatomic forces between coalescing islands or crystallites, or may be the filling up intergranular porosity.

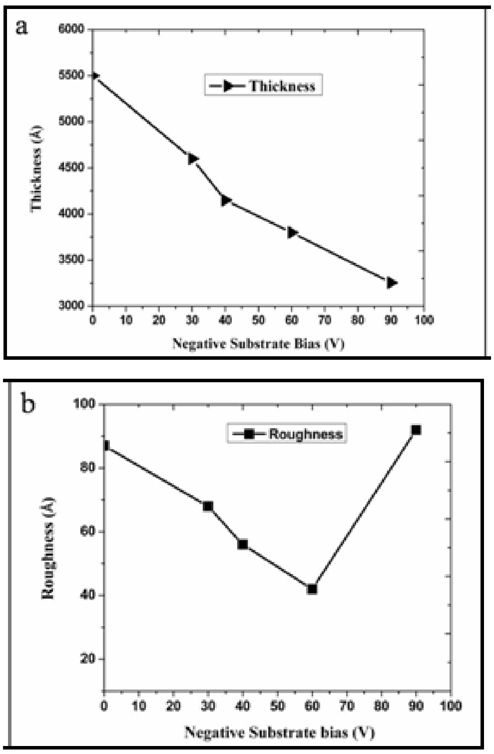


Figure 8: Variation of Residual stress of Ni-Ti-10%Cu films deposited at different (i) substrate temperature. (ii) substrate bias

Now for getting some more information on the shape memory properties of the materials some low temperature resistivity measurements have been done on the films. In Fig.9 the resistivity vs. temperature curve on heating cooling showed only one minimum, which suggests a cubic to orthorhombic single stage transformation (Ren *et al*., 2000). The very narrow hysteresis also suggests the applicability of the film as a shape memory material (Wang *et al*., 2002).

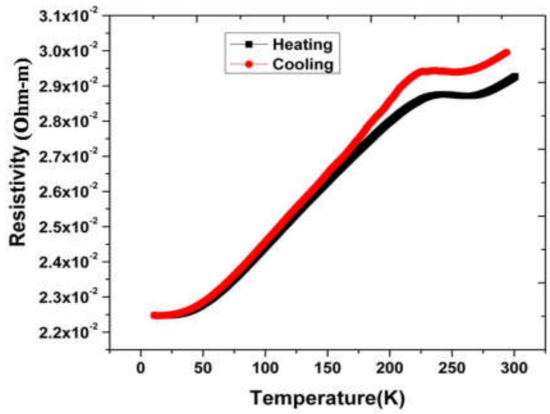


Figure 9: Resistance verses temperature plot of Ni-Ti-10%Cu films

Conclusions

Ni-Ti-Cu films were successfully deposited and characterized by various modern techniques. Results of the EDX showed that the chemical composition of Ti-Ni-Cu thin films was dependent on the DC power of pure copper, nickel target and the RF power of the titanium . Films deposited at high Ar gas pressure exhibited a columnar structure, while films deposited at a low Ar gas pressure showed smooth and featureless structure. Significant grain growth takes place with the different substrate temperature. Results from DSC and GIXRD revealed clearly the martensitic transformation of the deposited Ti-Ni-Cu films. The curvature measurement method also shows the dependency of the film stress with the substrate temperature and applied negative bias of the film. The AFM showed results that the moderate bias is required to minimize the film thickness. The resistivity versus temperature curve suggests that the film can be used for shape memory application. Further study on high temperature resistivity is very much needed in this regard.

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