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Structural and Electrical Properties of Titanium-Nickel Films Deposited onto
Silicon Substrates

by

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STRUCTURAL AND ELECTRICAL PROPERTIES OF TITANIUM-NICKEL FILMS DEPOSITED ONTO SILICON SUBSTRATES

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ABSTRACT

Thin films of the shape memory alloy NiTi have been sputter-deposited onto p-type silicon substrates. Films that are initially amorphous may be crystallized by vacuum annealing. The crystalline films exhibit the B2 $\rightarrow$ B19' phase change associated with the shape memory effect while remaining in contact with the silicon substrate. Transition temperatures were determined by resistance measurements and x-ray diffraction. The NiTi - Si contacts are diodes, as evidenced by their current-voltage characteristics; however, the effect of the phase change on the barrier height could not be determined.

INTRODUCTION

The intermetallic nickel-titanium alloy is the most common material exhibiting the shape memory effect [1]. A thermoelastic martensitic phase transformation provides the mechanism for the shape memory. In NiTi, the high temperature phase (austenite) has the CsCl, or B2, structure. An intermediate rhombohedral structure, the R - phase, has been identified. The low temperature phase (martensite) is monoclinic, and may exist in any one of twenty-four geometrically-related variants. Deforming martensitic NiTi interconverts these variants to whichever ones most reduce the internal energy. Upon heating, the NiTi must recover the high temperature structure. The only low energy pathway to the CsCl structure exactly retraces the atomic movements responsible for the deformation, and this causes the shape memory.

There has been growing interest in the fabrication of free-standing shape memory alloy films [2], and also in films that remain bound to a substrate [3]. The films prepared to date can be resistively heated to produce a mechanical response. They have been incorporated into the control element in microvalves and may prove useful as microactuators.

To our knowledge, semiconductor-metal structures have not previously been fabricated from NiTi films. Diodes constructed from such structures could in principle exhibit current-voltage properties reflecting the phase of the NiTi overlayer. In this paper we lay the groundwork for such a study by demonstrating that crystalline NiTi films can be deposited onto p-Si, yielding structures that exhibit rectifying behavior.

EXPERIMENTAL

NiTi films were prepared by standard d.c. magnetron sputtering from a composite NiTi target. Polished (100) p-type silicon substrates were chemically etched with a 10% solution of HF and rinsed with methanol prior to deposition. No intermediate or adhesion layers were deposited between the silicon and the NiTi. The films were annealed in sealed glass ampules, at 540°C under vacuum (10^{-3} torr), to initiate crystallization. Higher temperature annealing was not used because it is reported to cause precipitation within the metal film and reaction between the film and the

substrate, degrading the properties of the film [3,4]. It was also possible to crystallize films during deposition at temperatures less than 500°C [5].

The films were structurally and electrically characterized. Four-probe resistance measurements in a temperature-controlled chamber were made on the NiTi side of the sample. X-ray diffraction (XRD) powder patterns were taken on a Nicolet R3m/V Polycrystalline X-ray Diffraction System (Cu K α radiation), using a heated sample holder.

Auger electron spectroscopy measurements were performed on a Perkin Elmer Model 660 Scanning Auger Multiprobe; Ar⁺ sputter etching provided a depth profile of the films.

Electrical contacts for the current-voltage measurements were made by a spring-loaded pressure contact (NiTi side) and In/Ga eutectic (Si side).

CHEMICAL AND STRUCTURAL CHARACTERIZATION

The composition of the NiTi films was determined by Auger electron spectroscopy. All films show a surface titanium oxide, due to the high reactivity of titanium even with extremely low oxygen exposure. After annealing, this oxide layer becomes thicker, and carbon is also seen on the surface. Under the oxide layer, the films were composed entirely of nickel and titanium.

As-deposited films do not adhere well to silicon. The XRD patterns of as-deposited films were amorphous, showing only a very broad feature between $2\theta = 40^\circ$ - 45° and the silicon peak just under $2\theta = 80^\circ$. Since the shape memory effect is the result of a crystallographic phase change, resistance vs. temperature plots of the amorphous films were found to lack features characteristic of the phase change (vide infra).

After the annealing process, adhesion is dramatically improved, presumably due to reaction at the NiTi-Si interface. Once the films are annealed, the characteristic XRD pattern for NiTi is seen, along with the diffraction peak for silicon. The film resistance curves show the typical features of the phase transition (Fig. 1). As the sample is cooled from the austenite into the R-phase, the resistance rises sharply. When the film transforms from the R-phase into the B19' martensite, the resistance falls. Subsequent heating of the sample causes a gradual rise in resistance back to the austenite resistance. In some samples a small peak is seen in the heating curve as the NiTi transforms from the martensite.

The variable temperature XRD patterns also demonstrate the phase change (Fig. 2). In the austenite, a single large peak at $2\theta = 42.3^\circ$ appears. Cooling into the R-phase results in a splitting of this peak. As the martensite phase is reached, the most intense peak shifts to $2\theta = 42.5^\circ$, and its intensity shrinks by about half. A number of other B19' reflections appear at $2\theta = 39.2^\circ$, 41.2° , 43.8° , and 44.9° , indexed by Michal and Sinclair as the (020), (111), (002), and (111) peaks, respectively [6].

ANALYSIS OF THE RESISTANCE VS. TEMPERATURE PLOTS

Fourteen film samples having thicknesses between 0.5 and 8 microns were deposited onto silicon. Eight of them adhered during the annealing process, three detached before annealing, and three more detached during the anneal. Film thickness did not have a pronounced effect on adhesion. The three films that were detached before annealing were annealed as stand-alone foils for comparison to the substrate-bound films.



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Resistance vs. Temperature, NiTi Film on Si

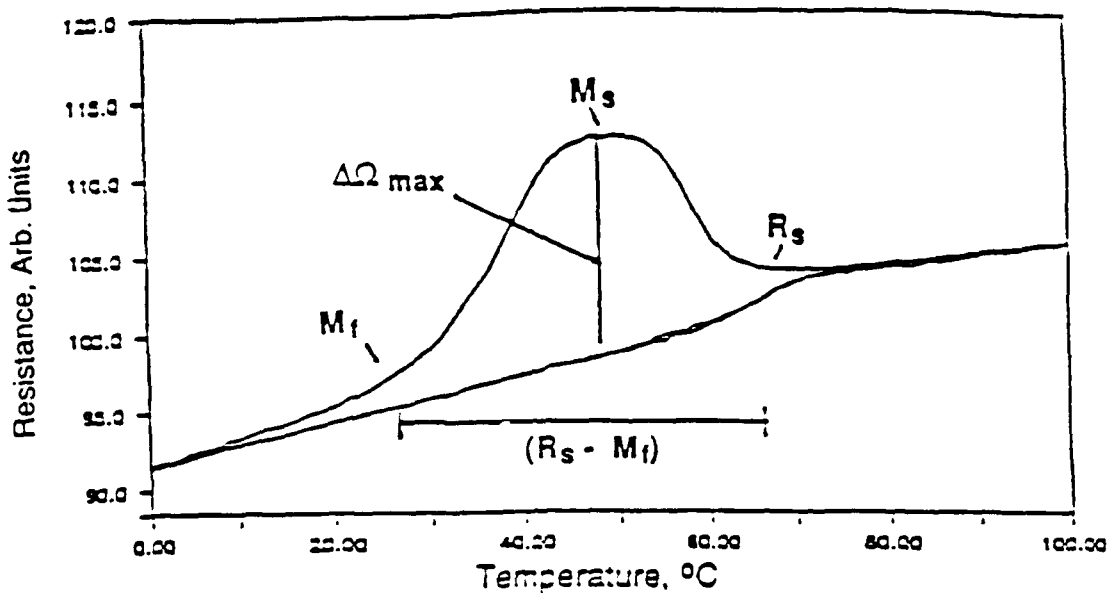


Fig. 1. A typical plot of film resistance vs. temperature. The transformation temperatures for the sample are labeled as follows: beginning of R-phase growth, R_s ; beginning of martensite growth, M_s ; and the end of the martensite transformation, M_f .

Variable Temperature XRD Powder Patterns of NiTi on Si

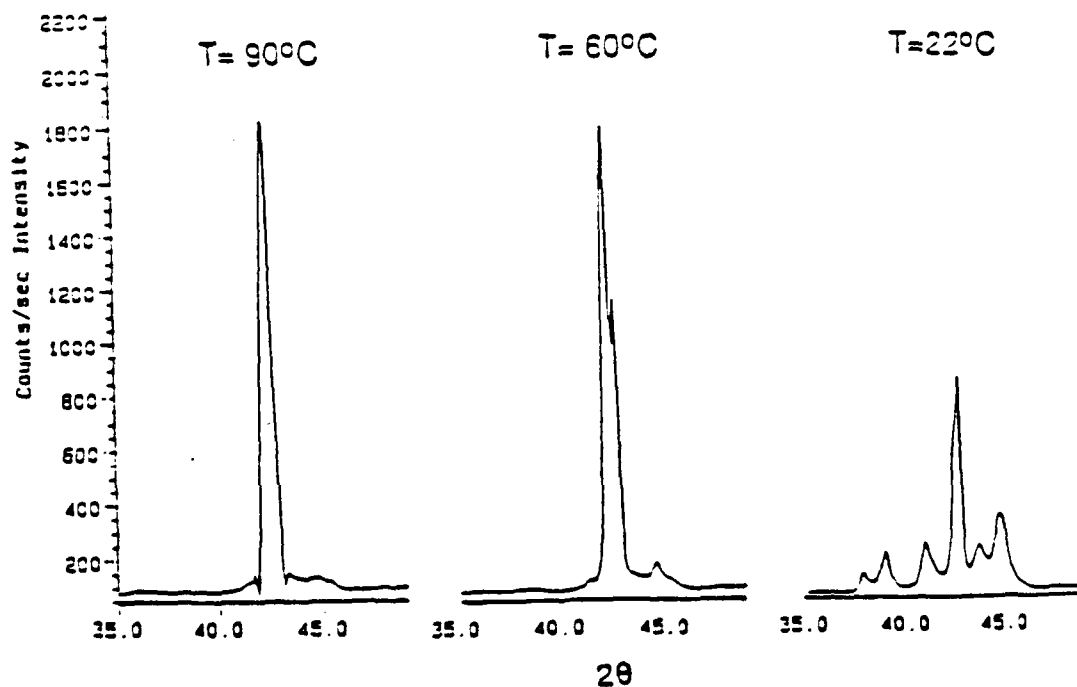


Fig. 2. The XRD powder patterns of NiTi on Si as it is cooled through the phase transformation. At $T = 90^\circ\text{C}$, 60°C , and 22°C , the NiTi is in the austenite phase, R-phase, and martensite phase, respectively.

The temperatures at which transformations into the R and martensite phases began, R_S and M_S , and the temperature at which the martensite transformation finished, M_f , were tabulated for each film, as was the total transformation width, $(R_S - M_f)$. The maximum difference in resistance at a particular temperature between the heating and cooling curves, $\Delta\Omega_{\max}$, was also determined for each sample. The parameters are shown on the resistance vs. temperature plot in Fig. 1.

The onset of the phase change during cooling occurred between forty and sixty-five degrees in most of the samples. The width of the transformation on cooling, $(R_S - M_f)$, was generally thirty to fifty degrees, although a few samples had much larger widths, between eighty and one-hundred degrees. Large values of $(R_S - M_f)$ were primarily due to a lower M_f temperature, since the M_S temperature fell between ten and thirty degrees below the R_S temperature regardless of the total width of the transformation. Values of R_S , M_S and $(R_S - M_f)$ could not be correlated with the film thickness.

The maximum change in resistance at a particular temperature, $\Delta\Omega_{\max}$, was a function of film thickness. Thicker films showed a larger absolute change in resistance. For samples taken from the same sputtering run, the change in the resistance is a linear function of thickness ($r^2 = 0.97$). The largest values of $\Delta\Omega_{\max}$ were found in samples that did not adhere to the substrate. Regardless of whether they became detached before or during annealing, they had values of $\Delta\Omega_{\max}$ that were, on average, 40% larger than those of the adherent samples.

Films under one micron in thickness generally had weak resistance signatures, showing only small changes in resistance as they were cooled.

CHARACTERIZATION OF NiTi-Si SCHOTTKY BARRIERS

The current-voltage (I-V) characteristics of the NiTi - Si junctions were measured. Like many metal - semiconductor contacts, they were capable of rectifying current. In the forward bias direction the film side acted as the cathode.

In order to measure the barrier height of the diodes, semilog plots of the I-V data were made (Fig. 3). However, the data were extremely curved, and it was not possible to extrapolate a value of the saturation current and therefore to calculate a value of the barrier height. Low temperature measurements extended the linear region, but it remained too small for accurate extrapolation.

Curvature of I-V data is often caused by a series resistance due to the semiconductor substrate. An alternative to the semilog I-V curve, introduced by Norde [7], allows the series resistance to be separated from the diode response. The following function is plotted vs. voltage:

$$F(V) = (V/2) - (k_B T/q) \ln (J/A^* T^2) \quad (1)$$

where J is the current density, A^* is the Richardson constant ($32 \text{ A/cm}^2 \text{K}^2$) for p-type Si, T is the temperature, and k_B and q have their usual values. The barrier height is calculated from the minimum in the $F(V)$ curve, so long as the minimum occurs at a voltage greater than $3k_B T/q$. For all samples tested, there was either no minimum in the Norde plot, or the minimum was below $3k_B T/q$. This indicates that the series resistance probably is not the cause of the curvature.

Although the NiTi - Si junction acts as a diode, its properties are far from ideal. At high voltages ($>1\text{V}$) the semilog I-V curves are linear, and the ideality constant, n ,

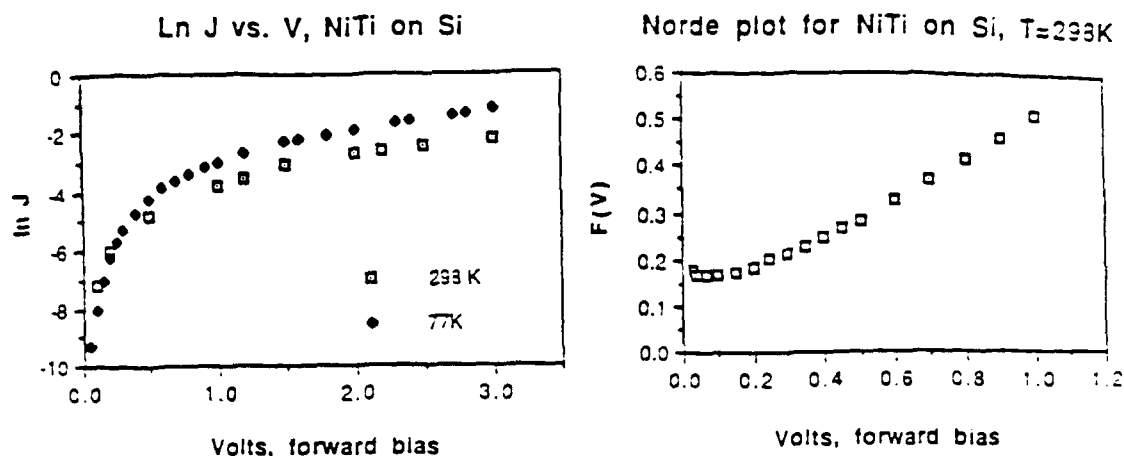


Fig. 3. Two methods of analyzing current-voltage data in the forward bias direction are shown. On the left, $\ln(J)$ is plotted against the applied voltage. On the right, a sample Norde plot (equation 1) is presented.

may be calculated from the slope of the line in this region using the I-V relationship for thermionic emission:

$$J = J_0 [\exp(qV/nk_B T)] \quad (2)$$

This equation applies for voltages greater than $3k_B T/q$. Values of n ranged from 5 to 50 for the NiTi - Si contacts, all well above the ideal value of 1.02. This may indicate the presence of a large interfacial layer between the NiTi and Si, or that current transport mechanisms in addition to thermionic emission are in effect.

CONCLUSIONS

NiTi films can be deposited directly onto silicon. The NiTi is amorphous upon deposition and shows no phase change. After annealing, the martensitic phase change that creates the shape memory effect is observed in the films, and temperature cycling does not cause the film to become detached from the silicon substrate.

The width of the phase change is generally 30 to 50 degrees, and the R_s temperatures, indicating the beginning of the phase change while cooling, ranged from 45 to 65 degrees. Extremely wide transitions, larger than 80°C, were due to low M_f temperatures. Film thickness did not appear to affect any of the transition temperatures, but the value of $\Delta\Omega_{\max}$ was a function of thickness.

The NiTi - silicon junctions are capable of rectifying; however, a barrier height could not be extracted from the current-voltage curves. Lower temperature annealing methods to limit the growth of interfacial layers are currently being explored to improve the quality of the diodes and to determine the dependence of diode properties on the phase change in the NiTi films.

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REFERENCES

1. K. R. Collen et al., "Principles of the Shape Memory Effect in Nickel-Titanium" in Chemistry of Advanced Materials, ed. by C.N.R. Rao (Blackwell, in press).
2. J. A. Walker et al., Sensors and Actuators A, 243 (1989).
3. A.P. Jardine et al., unpublished results.
4. M. Berkson, J. D. Busch and A.D. Johnson, these proceedings
5. K R. Collen, A. B. Ellis, J. D. Busch, and A.D. Johnson, in preparation.
6. G.M. Michal and R. Sinclair, Acta Cryst. B37, 1803 (1981).
7. H. Norde, J. Appl. Phys. 50, 5053 (1979).

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