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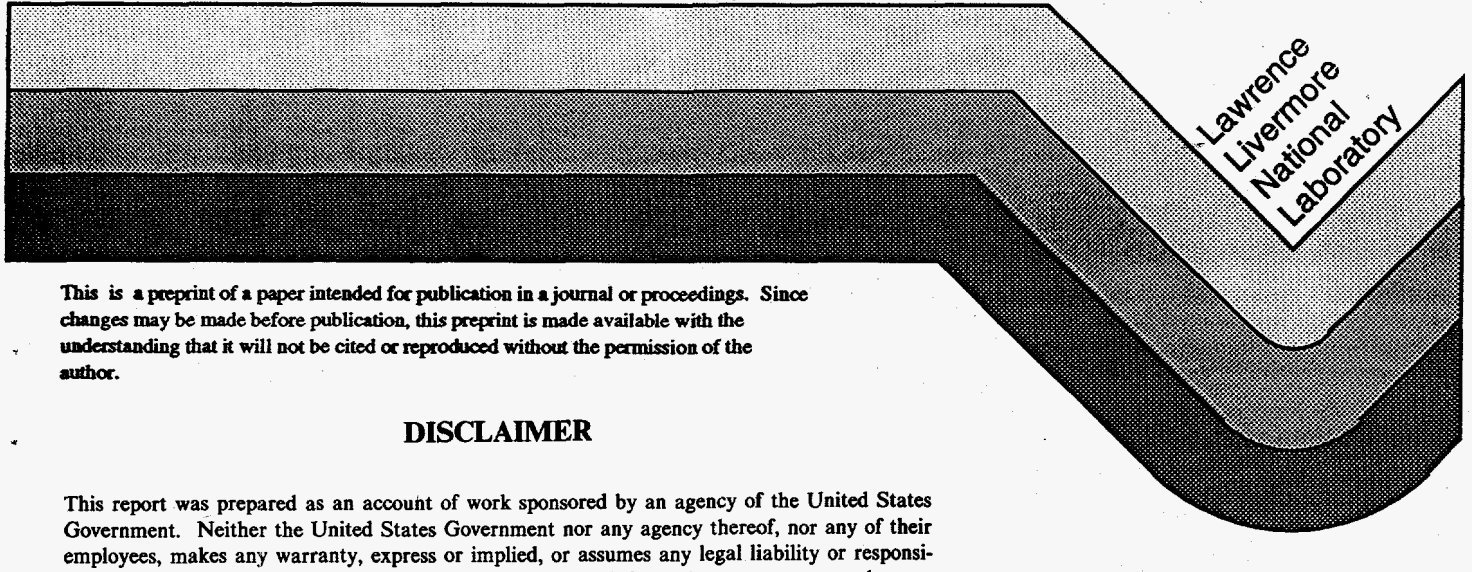

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SYNTHESIS AND CHARACTERIZATION OF NANOPHASE FACE-CENTERED-CUBIC TITANIUM

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Abstract *-- Unalloyed Ti is sputter deposited in the formation of two trilayer films. Each layer within the combinations of Ni-Ti-Ni and Ti-Ni-Ti is less than 0.1 μm thick. High resolution imaging and electron diffraction results are presented for the microstructural characterization of both trilayer films. Nanophase fcc Ti is initially found in crystalline layers grown on Ni whereas hcp Ti is found in layers grown without a Ni epilayer. Conditions are further examined under which the fcc to hcp transition occurs for Ti deposited on Ni.*

INTRODUCTION

The equilibrium phases of unalloyed Ti are hcp (at low temperature) and bcc (at high temperature). An fcc phase of Ti can be synthesized using the physical vapor deposition processes of sputtering and evaporation. The fcc Ti phase is known to form as an ultrathin layer on cleaved NaCl substrates (1-3) and as discrete layers within multilayer structures as Ni/Ti (4-7) and Al/Ti (8,9). The stabilization of the fcc Ti phase is attributed to (i) epitaxial growth (1-5), (ii) through the incorporation of hydrogen and/or oxygen as gas impurities during growth (6) and (iii) as a low-temperature phase transformations from an hcp parent phase (8). For the samples of this study, stabilization by gas impurities is not the case as confirmed by the growth of hcp Ti without a Ni epilayer, for the identical vacuum deposition conditions as used to form the fcc phase with a Ni epilayer.(5) The presence of both the hcp and fcc phases of Ti are reported for layer thickness >15 nm in Ni/Ti multilayers.(7) Diffraction analysis of Ni/Ti multilayers reveals lattice strain within the layers along the growth direction.(10) Misfit strains, i.e. the distorted lattice spacings, are modeled and found to approach bulk values away from the interfaces. Therefore, providing the Ti layers are thick enough, the epitaxial fcc phase should become unstable and revert to the equilibrium hcp phase. The intial study of fcc Ti phase stabilization in Ni/Ti multilayers (4,5) is continued through use of a trilayer structure. We will provide further evidence of epitaxial stabilization of fcc Ti and assess the layer location(s) for which growth of the fcc phase becomes unstable.

EXPERIMENTAL PROCEDURE

The trilayer structures are prepared using sputter deposition. Planar magnetrons are operated in the dc mode using a working gas of argon at a 0.40 Pa pressure and 15.9 cc min^{-1} flow. The vacuum chamber base pressure is 1.0×10^{-6} Pa. The 0.9994 pure Ni and Ti targets are 0.5 cm thick with a 6.4 cm diameter. The Si wafer substrates are attached to a Cu platen which is positioned 17 cm above the collimated magnetron sources. The substrate temperature

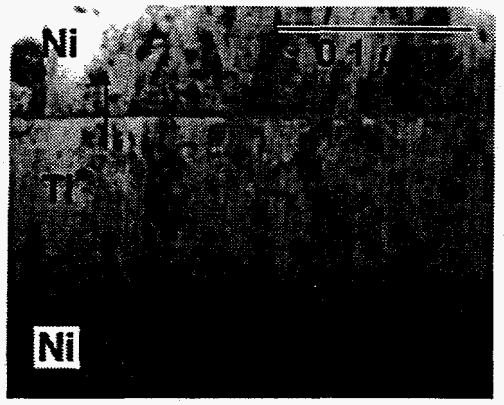

Fig. 1 - A bright field image of the Ni-Ti-Ni trilayer viewed in cross-section.

Fig. 2 - A bright field image of the Ti-Ni-Ti trilayer viewed in cross-section.

is monitored and remains at 308-313 K during the deposition. The substrates are alternately shuttled over the Ni and Ti sputter sources to produce trilayer deposits of Ni-Ti-Ni and Ti-Ni-Ti. The Ti source is operated at a 266 V discharge and 1.35 amps to produce a 0.051 nm sec^{-1} deposition rate. Similarly, the Ni source is operated at a 340 V discharge and 0.15 amps to produce a 0.042 nm sec^{-1} deposition rate. Contact profilometry is used to calibrate the deposition rates and confirm the total thickness of each trilayer deposit. The nominal thicknesses for the Ti and Ni component layers are 91 and 75 nm, respectively.

The trilayer microstructures are characterized using a transmission electron microscope (TEM). Samples are prepared for TEM imaging using the following basic procedure to cross-section the trilayer samples. Two slices of the trilayer-coated substrate are epoxied face-to-face then inserted into a 3mm diameter tube. Thin sections are cut from the tube using a diamond saw. The discs are lapped to thin the section from a 0.30 mm thickness to 0.10 mm. Next, a dimpling machine is used to produce a concave impression in the sample which is then finally ion-milled in a cold-stage. In the figures to follow, the film growth direction is always indicated with an arrow. TEM bright field (BF) imaging reveals growth morphology and grain size. High resolution TEM imaging at the Scherzer defocus condition provides a view of the atomic positions within the lattice structure. TEM selected area diffraction pattern (SADP) analysis reveals film texture and lattice symmetry. Microdiffraction is accomplished using a 40 ± 10 nm beam size to probe the Ni and Ti component layers individually, in order to provide element specific, crystallographic phase identification. Details of the procedures used to differentiate the fcc phase from the hcp phase of Ti through analysis of the diffraction patterns and high resolution images are found elsewhere.(4,5) In the following section, results using the detailed analysis procedure are presented for the trilayer structures.

EXPERIMENTAL RESULTS

The BF images of the cross-sectioned trilayers (Figs. 1 and 2) reveal a dense columnar structure which is typical for sputtered thin film deposits. The typical grain size, i.e. column width, is 30 to 40 nm. The growth morphology is nodular as evidenced by the convex shape to the termination of each column within a layer. This morphology corresponds to growth conditions with near-thermalized sputter neutrals.(12) This growth mode hinders the tendency

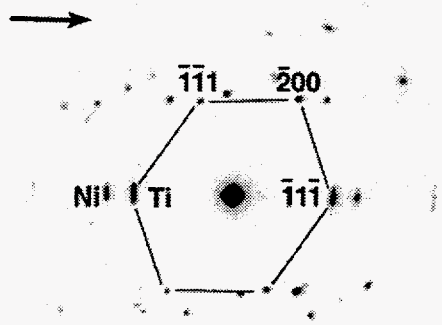

Fig. 3 - A SADP of the Ti layer in the Ni-Ti-Ni structure viewed in cross-section.

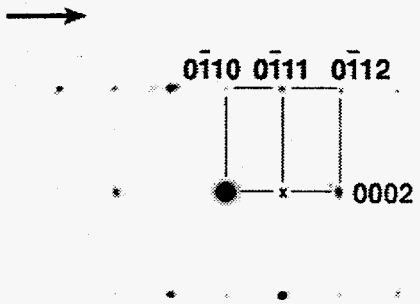

Fig. 4 - A SADP of the bottom Ti layer in the Ti-Ni-Ti structure viewed in cross-section.

towards interface phase formation as a consequence of an energetic deposition process. Consequently, both the Ni-Ti and the Ti-Ni interfaces of the trilayer deposits are expected and found to be crystalline rather than amorphous.(13)

The crystalline phase of the Ti layer in the Ni-Ti-Ni trilayer is identified from the SADP (Fig. 3) corresponding to the cross-section (Fig. 1). An fcc Ti diffraction pattern is superposed on the characteristic fcc Ni(111) pattern. Twinning within the Ti layer is evident along the growth direction. There is no indication of a hcp pattern, as Ti(0002) for this sample. Whereas the Ti layer has a (111) textured growth, the grains are randomly oriented in-plane as is typical for sputter deposited thin films. The random in-plane orientation is evidenced in the contrast from grain to grain as seen in the BF image (Fig. 1).

The phase(s) of Ti in the Ti-Ni-Ti trilayer are examined using microdiffraction. The bottom layer has a diffraction pattern (Fig. 4) characteristic of hcp Ti(0002). The growth of hcp Ti has occured without the Ni epilayer. In the top Ti layer, an fcc growth (Fig. 5) has originated from the Ni layer as seen for the Ti layer in the Ni-Ti-Ni structure. The fcc Ti(111) growth

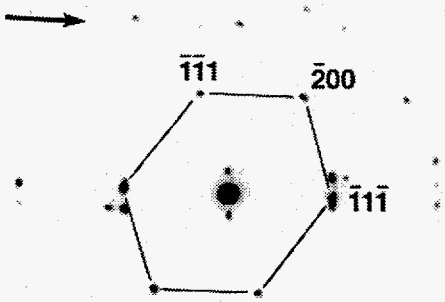

Fig. 5 - A SADP of the top Ti layer in the Ti-Ni-Ti structure viewed in cross-section.

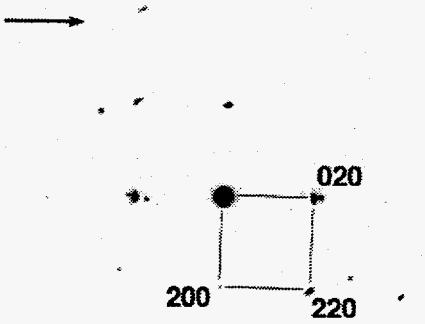

Fig. 6 - A SADP of the top Ti layer in the Ti-Ni-Ti structure viewed in cross-section.

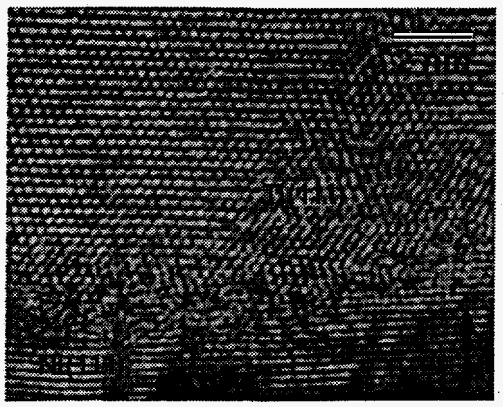

Fig. 7 - A high resolution image of the top Ti layer in the Ti-Ni-Ti structure cross-section.

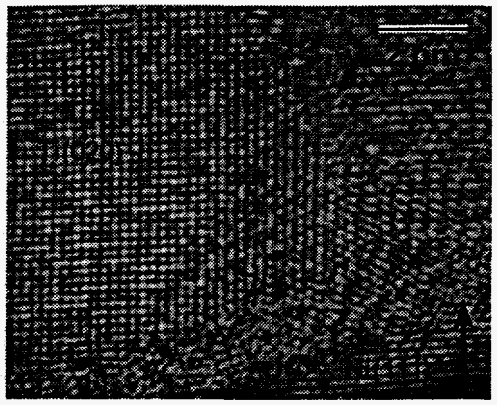

Fig. 8 - A high resolution image of the top Ti layer in the Ti-Ni-Ti structure cross-section.

orientation was typical. However, a second type of fcc Ti growth is found above the Ni layer. A fcc Ti(020) textured growth (Fig. 6) is evident in the SADP(s) from regions of roughness and/or high curvature, i.e. typically above the columnar boundaries of the Ni layer. The fcc Ti(020) growth mode is found in less than 20% of the SADPs taken from the top Ti layer.

High resolution imaging of the trilayer systems facilitates identification of where the phase formations and transitions are found within the Ti layering. In addition, regions were the texture of the fcc Ti growth changes can be correlated with locations above the Ni layer that correspond with curvature. As found in lattice images of the Ti-Ni-Ti trilayer, flat areas induce <111> growth (Fig. 7) whereas curved regions also stabilize a <020> growth (Fig. 8).

It is difficult to ascertain where an fcc-to-hcp transition occurs within a Ti layer. No conclusive evidence is found in SADPs, i.e. we have not found hcp patterns in Ti layers deposited on Ni layers. However, in the high resolution images of Ti-on-Ni, the presence of hcp Ti is occasionally found in two different locations. The first is within the Ti layer 50 to 60 nm above the Ti-Ni interface adjacent to columnar boundaries within the Ti layer. This location within the top Ti layer is perhaps where the greatest extent of structural disorder occurs allowing the fcc phase to relax to an hcp phase. A change in the stacking sequence from an ABCABC fcc Ti(111) growth mode is seen to an ABAB sequence (Fig. 9) typical for hcp Ti(0002). The second location of hcp Ti occurs at Ti-Ni interfaces where the structure has amorphized during growth as seen in this isolated region within the Ni-Ti-Ni trilayer structure (Fig. 10).

DISCUSSION & SUMMARY

The epitaxial growth of fcc Ti on Ni is found in the Ni-Ti-Ni and Ti-Ni-Ti trilayers, as is the case for the Ni/Ti multilayers(4,5), where the texture and crystalline structure of the Ni layer servea as a template for the Ti layer. The growth of hcp Ti(0002) is a natural crystalline growth for Ti without a Ni epilayer as has been previously shown.(5) The hcp growth mode is also seen at Ti-on-Ni interface locations where the structure has, in all probability, amorphized during the deposition. In addition, at thicknesses >50-60 nm, the appearance of hcp Ti is found within the fcc Ti layer of the Ti-Ni-Ti structure. It is clear that the SADP(s) represent the general trends of growth for each Ti layer with respect to crystalline phase and orientation, whereas small regions of hcp Ti can go undetected.

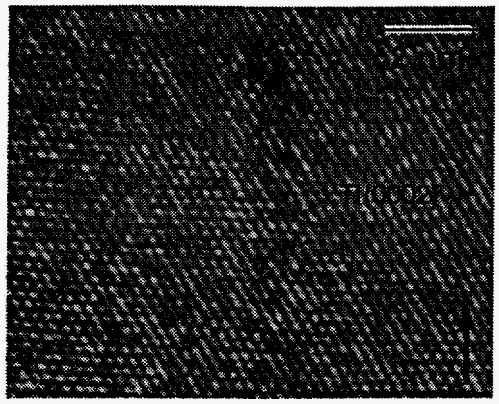

Fig. 9 - A high resolution image of the top Ti layer in the Ti-Ni-Ti structure cross-section.

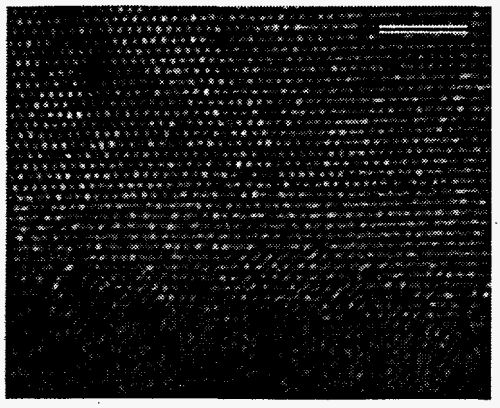

Fig. 10 - A high resolution image of the middle Ti layer in the Ni-Ti-Ni cross-section.

In summary, deposition conditions effect the growth of metastable phases, as fcc Ti. We have found the stabilization of fcc Ti as an overgrowth on fcc Ni. The appearance of hcp Ti occurs without Ni and at locations of structural disorder (as amorphous interfaces) and relaxation (as >50-60 nm above the epitaxial interface).

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