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Formation of intermetallic phase in Ni/Ti multilayer structure by ion implantation and thermal annealing

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ABSTRACT

Ion implantation and thermal annealing effects on composition and structure of Ni/Ti multilayer have been studied and reported in this paper. The thin films composed of five (Ni/Ti) bilayers were deposited by d.c. ion sputtering on (100) Si wafers to a total thickness of ~180 nm. Ion irradiations were performed by 180 keV Ar^+ ions with fluence of 6×10^{16} ions cm^{-2}. After deposition and implantation, the samples were annealed at 400 °C for 30 min in an inert ambient. Composition and structural characterizations were performed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). Annealing of as-deposited samples at 400 °C induces a progressed interaction between Ni and Ti layers with the initial formation of NiTi alloy phase. Progressed alloying was achieved for the ion fluence of 6×10^{16} ions cm^{-2} and the formed structure is composed of NiTi compound, only at depth around the projected ion range. In the deeper layers, beyond the projected range of implanted ions, the diffusion of Ni atoms can lead to solid state amorphization. Subsequent annealing at 400 °C for 30 min enabled enhanced interaction between intermixed Ni and Ti layers, and in the layers close to the Si substrate the conditions for the formation of intermetallic compound are created.

1. Introduction

Metallic multilayer coatings made by combining the appropriate layers at nanometer domain have shown a significant improvement of their performances in relation to each individual layer [1–3]. Thin film multilayer structure exhibits many new chemical, structural, electrical, magnetic, optical and transport properties. The Ni/Ti multilayer system has attracted special interest in its applications in various technologically important areas. The Ni/Ti multilayer structure is found to be useful in the field of soft X-ray and neutron optics because of their excellent contrast factor of thermal and cold neutrons. This multilayer Ni/Ti thin film is a combination of magnetic and non magnetic materials and it is suitable for polarization neutrons. They are ideal candidates for optical components such as supermirror, polarizers, monochromators, etc [4,5].

When using the Ni/Ti multilayer structure as functional thin films, in some cases it is necessary to make the intermetallic compounds (first TiNi, but also $TiNi_3$, Ti_2Ni, etc.) with the specific unusual physico-chemical properties. Nickel – titanium (NiTi) shape memory alloy (SMA) is a relatively new material that has attracted immense research interest for biomedical and micro-actuators application [6,7]. The combination of excellent biocompatibility, good corrosion resistance, good strength and ductility with specific functional properties of shape memory effect and superelasticity creates a smart material for its applications in medical and engineering fields [8].

Multilayer structure in form of thin films is inherently metastable state and susceptible to the thermal degradation. Many processes such as interdiffusion, intermixing, electron density gradation, chemical phase formation, etc. are activated in the multilayer structure due to thermal treatment. The NiTi intermetallic compounds can be synthetized from multilayer structure by solid state reaction at temperatures above 400 °C [9,10]. Ion implantation is particularly interesting due to the possibility that any element can be built into a solid target. Concentration and distribution of implanted ions could be achieved in the target, which is cannot be obtained by other methods. Ion beam synthesis (IBS) is a special method for the synthesis of new phases by

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implantation of high ions fluences in the sub-surface area of the target. Some of the advantages of IBS method compared to Molecular Beam Epitaxy (MBE) and Chemical Vapor Deposition (CVD) are: precise control of depth and thickness of implanted ions, formation of compounds of high purity by solid state reaction, synthesis of metastable phases due to non-equilibrium process of the ion implantation and the low temperature treatments of the materials [11]. In addition to thermal annealing, ion implantation of inert gases can induce intermixing in the multilayer structure and the formation of new phases which is impossible to produce by other conventional methods [12,13].

From the viewpoint of material science, there are many reports on unique features of TiNi alloy, ranging from the physical and chemical properties to biological performance [4–7]. In the present article, we have investigated the effects of argon ion implantation and thermal annealing on the composition and structural properties of sputter deposited Ni/Ti multilayer thin films on Si substrate. The aim was to study intermixing of Ni and Ti layers to achieve intermetallic phases. The main objective of the present work was to examine the joint influence of ion implantation and subsequent annealing at the lower temperature for the formation of intermetallic compounds on the behavior of Ni/Ti multilayer system.

2. Experimental details

The Ni/Ti multilayer structures were prepared by a commercial Balzers Sputtron II vacuum system using 1.5 keV argon ions and 99.9% pure Ni and Ti targets. The depositions was carried out under the base pressure in the chamber around 1×10^{-6} mbar and argon partial pressure during deposition 1×10^{-3} mbar. The substrates used were n-type silicon (100) wafers (0.5 mm thick) held at ground potential. They were cleaned by an HF etch and dip in deionized water before mounting in the chamber. Prior to layer deposition, the substrate was additionally cleaned by back-sputtering. Multilayers were deposited in a single vacuum run at $\sim$0.13 nms^{-1} for Ni and $\sim$0.1 nms^{-1} for Ti, without heating the substrates. The deposited multilayer structures consisted of ten alternate Ni and Ti layers, five of each, with total thickness of 180 nm. The first layer deposited on the substrate was Ti and the outermost Ni. Post-deposition thermal annealing of the samples was performed at temperature of 400 °C for 30 min in an inert ambient.

Ion irradiation of samples was done using DANPHYSIC ion implanter, with 180 keV Ar^+ ion beam at normal incidence. The beam was uniformly scanned over a target area 2.5×2.5 cm^2 and the implanted fluence was 6×10^{16} ions cm^{-2} for argon implantation. The implantation was performed at room temperature, the beam current density being maintained at $\sim$1 μA cm^{-2} to avoid beam-heating of the samples. The projected range of the implanted ions is near the middle of the multilayered structure, calculated with SRIM [14].

The phase composition and crystalline structure of the Ni/Ti multilayer samples was studied by X-ray diffraction (XRD). Measurements were carried out on a standard Bruker D8 Diffractometer with parallel beam optics using Cu K_α diffraction patterns. Angle 2θ was scanned in the range from 35° to 60° at step of 0.02°, in time sequence of 10 s. Compositional analysis of (Ni/Ti)x5/Si system was done by X-ray photoelectron spectroscopy (XPS) in the PHI-TFA XPS spectrometer. XPS spectra were excited by X-ray radiation from an Al-standard and an Al-monochromatic source. The relative sensitivity factors 2.08 for Ti 2p, 1.23 for Ar 2p, 0.37 for Si 2p, 0.31 for C 1s and 0.733 for O 1s, provided by instrument producer were used to calculate surface concentrations [15]. We used the relative sensitivity factor for the Ni $2p_{3/2}$ peak of 5.73, which was determined from the signal of pure Ni layer in the as-deposited Ni/Ti multilayer. Accuracy in the binding energy position of peaks in the XPS spectra was about 0.2 eV. Carbon C 1s spectrum from surface contamination layer was used to align the energy scale in the XPS spectra at 284.8 eV. Transmission electron microscopy (TEM) was done on a Philips EM 400T microscope and High Resolution TEM Joel JEM-200 microscope. Electron diffractions were done on an HRTEM microscope (model Philips CM 200) operated at 200 keV. The samples were prepared for cross-sectional and plane-view analysis by standard technique of ion beam thinning.

3. Results and discussion

3.1. X-ray diffraction analysis

The results of XRD analysis are given in Fig. 1. for the following samples: (a) as-deposited (Ni/Ti)x5/Si, (b) annealed at 400 °C, (c) implanted with Ar^+ ions to 6×10^{16} ions cm^{-2} and (d) sample modified by both implantation and annealing at same conditions. The XRD pattern (Fig. 1a) corresponding to the as-deposited (Ni/Ti) x5/Si multilayer sample shows two well-defined diffraction peaks which can be assigned to face-centered cubic (fcc) structure of Ni (111) plane at $2\theta = 44.35°$ and hexagonal close packed (hcp) structure of Ti (002) plane at $2\theta = 38.46°$. The big difference among

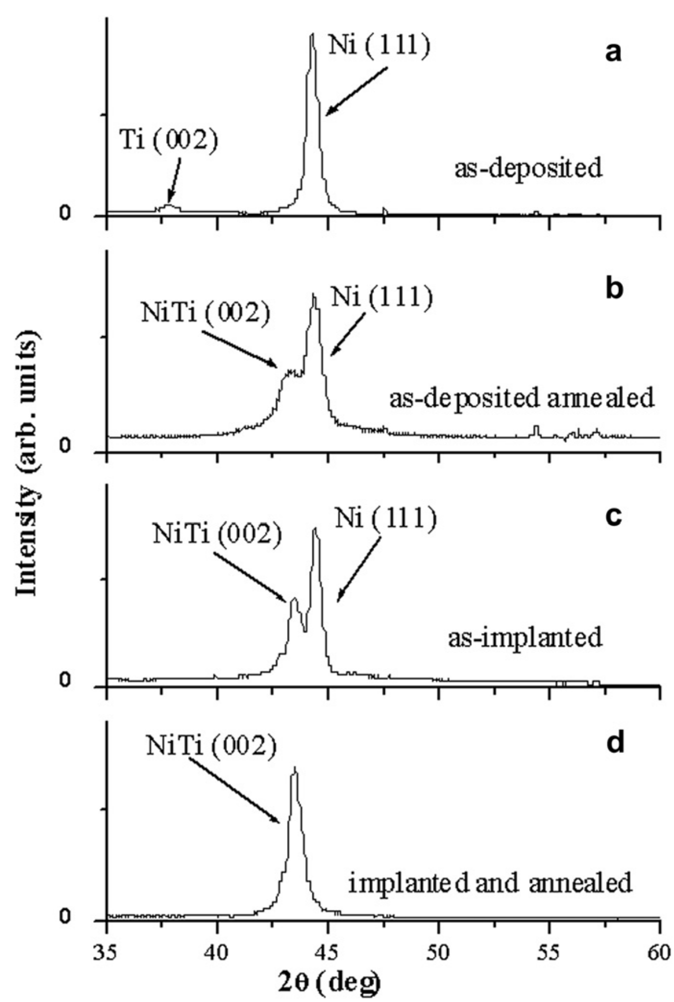

Fig. 1. XRD spectra of the (Ni/Ti)x5/Si multilayer structure: (a) as-deposited, (b) annealed at 400 °C, (c) as-implanted with Ar^+ ions to 6×10^{16} ions cm^{-2}, and (d) Ar-ion implanted and annealed samples.