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Solid-state Reactions in Ni/Si Multilayered Films, Investigated by Optical and Magneto-optical Spectroscopy

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Abstract

Solid-state reactions in Ni/Si multilayered films (MLF) with an overall stoichiometry of Ni_2Si, NiSi and $NiSi_2$, induced by ion-beam mixing (IBM) and thermal annealing, were studied by using spectroscopic ellipsometry and magneto-optical spectroscopy as well as x-ray diffraction (XRD). The mixing was performed with Ar^+ ions of an energy of 80 keV and a dose of 1.5×10^{16} Ar^+/cm^2. It was shown that the IBM induces structural changes in the Ni/Si MLF, which cannot be detected by XRD but are confidently recognized by the optical method. A thermal annealing at 673 K of the Ni/Si MLF with an overall stoichiometry of NiSi and $NiSi_2$ causes formation of the first η-NiSi phase. The first trace for $NiSi_2$ phase on the background of NiSi one was detected by XRD after an annealing at 1073 K while, according to the optical results, $NiSi_2$ turns out be the dominant phase for the annealed Ni/Si MLF with an overall stoichiometry of $NiSi_2$.

Keywords : Multilayered films, Ion-beam mixing, Silicide, Optical conductivity

1. Introduction

Interlayer solid-state reaction in 3d transition metal / Si multilayered films (MLF) during deposition is an intriguing problem. An amorphous phase of η-NiSi may be formed owing to the interlayer mixing in Ni/Si MLF [1] and various other silicides can be formed. The Ni silicide formation, caused by thermal annealing of Ni films deposited onto a Si wafer, is a consequence of the free-energy decrease in such a reaction and a certain external energy input can accelerate substantially the silicide formation by changing the thermodynamic energy of the system. An annealing of polycrystalline Ni films, with a thickness of 100 - 500 nm, deposited onto a single-crystalline Si substrate leads to, firstly, the formation of Ni_2Si phase after the annealing at 473 - 600 K and to the η-NiSi phase after the annealing at 873 K [2]. The employment of an ion-beam mixing (IBM) for the silicide formation implies that the two layers can be interacted by the energetic incoming particles in such a way that cannot be achievable by the usual equilibrium techniques. It is well known that both optical and magneto-optical (MO) properties of metals depend strongly on their electron energy structures, which are correlated with the atomic ordering in the reactive zone as well as a decrease in the thickness of pure Ni.

2. Experiment

Three kinds of Ni/Si MLF were prepared by dc magnetron sputtering onto single-crystalline Si substrates at room temperature (RT): $(3\ nm\ Ni/2.69\ nm\ Si)_{40}$, $(3\ nm\ Ni/5.37\ nm\ Si)_{50}$, and $(3\ nm\ Ni/10.7\ nm\ Si)_{22}$ MLF. The

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individual sublayer thicknesses were chosen to be thinner than skin-penetration depth.

The structural characterization of Ni/Si MLF was performed by low-angle x-ray diffraction (LAXRD). The magnetic state of the as-deposited Ni/Si MLF was checked by investigating the in-plane and the out-of-plane magnetization hysteresis loops, M(H), at RT, which were obtained with a vibrating sample magnetometer. The optical properties were studied at RT by spectroscopic ellipsometry [3]. The MLF were ion-beam mixed in a high vacuum ($\sim 1\times10^{-6}$ Torr) by Ar^+ ions directed normally to the film surface with the following conditions: an ion energy of 80 keV, an ion flux of 1.5×10^{-6} A/cm^2, and an ion dose of 1.5×10^{16} Ar^+/cm^2. Additionally, the as-deposited Ni/Si MLF were annealed in series at 453, 683, 823 and 1073 K and the physical properties were also studied after each step of annealing.

3. Results and Discussion

The optical-conductivity (OC : σ) spectra for the as-deposited Ni/Si MLF with relatively thin Si sublayers and overall stoichiometry of Ni_2Si and NiSi exhibit a gradual increase in the magnitude with increasing photon energy, showing a feature at $\hbar\omega$=2 eV (see Figs. 1 and 2). The OC spectrum for the as-deposited (3.0 nm Ni/10.7 nm Si)$_{22}$ MLF show a prominent absorption peak at about 3.3 eV (see Fig. 3). The optical properties of amorphous Si as well as polycrystalline Ni have been well investigated [4,5].

The simulated OC spectra for all the Ni/Si MLF look similar to each other, exhibiting a prominent absorption peak near 3.1 - 3.3 eV, and are different insignificantly in the magnitude and the location of maximum (see

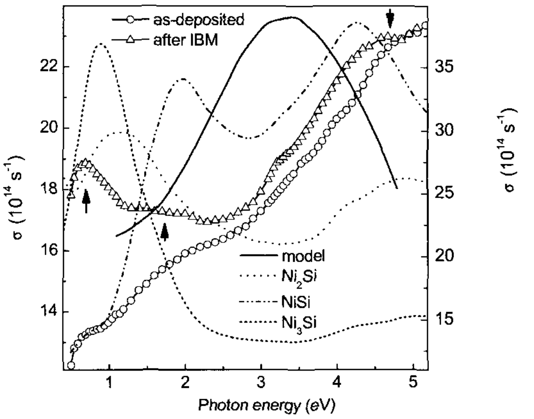

Fig. 1. Experimental OC spectra for the as-deposited and the ion-beam mixied(3.0 nm Ni/2.69 nm Si)$_{40}$ MLF (left scale). The modelled OC spectrum for this MLF, together with the literature data for NiSi, Ni_2Si and Ni_3Si, are also shown for the comparison (right scale).

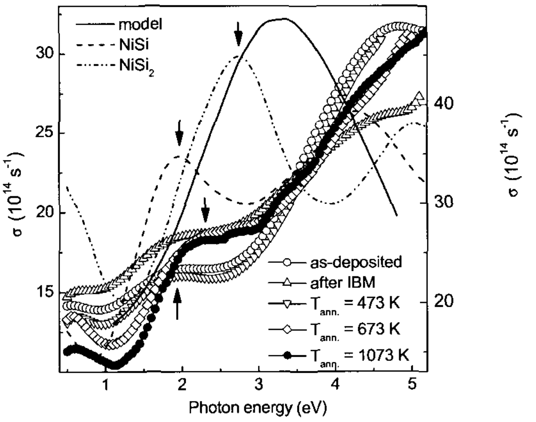

Fig. 2. Experimental OC spectra for the as-deposited, the ion-beam mixied and the annealed (3.0 nm Ni/5.37 nm Si)$_{50}$ MLF (left scale). The modelled OC spectrum for this MLF, together with the literature data for NiSi and $NiSi_2$, are also shown for the comparison (right scale).

Table 1. Sample list.

Nominal sample formula	Sample formula according to LAXRD	Measured sample formula	Actual composition
30 A Ni/26.9 A Si	39 A Ni/41 A Si	43 A Ni/39 A Si	$Ni2Si/Ni_{0.668}Si_{0.332}$
30 A Ni/53.7 A Si	37 A Ni/67 A Si	36.5 A Ni/67.5 A Si	$NiSi/\ Ni_{0.497}Si_{0.503}$
30 A Ni/107 A Si	39 A Ni/139 A Si	39 A Ni/139 A Si	$.5NiSi2/Ni_{0.349}Si_{0.651}$

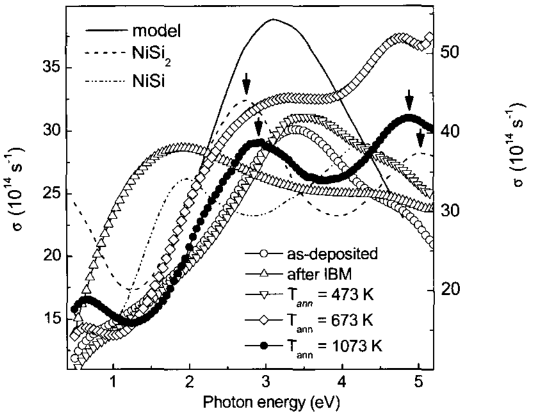

Fig. 3. Experimental OC spectra for the as-deposited, the ion-beam mixied and the annealed (3.0 nm Ni/10.7 nm Si)$_{22}$ MLF (left scale). The modelled OC spectrum for this MLF, together with the literature data for NiSi and NiSi$_2$, are also shown for the comparison (right scale).

Figs. 1-3). The absence of any visible trace of this absorption peak in the experimental OC spectra of the as-deposited Ni/Si MLF with an overall stoichiometry of Ni_2Si and NiSi enables us to suppose the lack of pure Si content in such films due to, for example, the Si consumption for the Ni-silicide formation. This is consistent with a statement by Clevenger and Thompson that, in the as-deposited Ni/Si MLF, an amorphous NiSi phase of about 4-nm thick is formed between polycrystalline Ni and amorphous Si sublayers [6]. It is also seen that a rather reasonable coincidence in the shape between the simulated and the experimental OC spectra is observed only for the Ni/Si MLF with the thickest Si sublayers (see Fig. 3). The IBM does not produce any visible change in the OC spectrum of (3.0 nm Ni/6.75 nm Si)$_{50}$ MLF with an overall stoichiometry of NiSi (see Fig. 2). The OC spectrum after the IBM shows a peculiarity at $\hbar\omega=2$ eV. Thermal annealings at different temperatures of the MLF causes gradual changes in the optical properties towards those of the crystalline NiSi. Each step of annealing makes the interband absorption peak at $\hbar\omega=2$ eV more evident. Such a process illustrates an improvement in the crystallinity of the NiSi phase.

4. Conclusions

The optical tools were applied to investigate the solid-state reaction in the Ni/Si MLF. The comparison of the experimental OC spectra of the Ni/Si MLF, as-deposited or post-treated, with those of the bulk Ni silicides enables us to conclude that amorphous regions with a stoichiometry close to NiSi are spontaneously formed during the deposition of Ni/Si MLF.

Acknowledgments

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