First stages of the formation of Ni silicide by atom probe tomography

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(Received 18 April 2006; accepted 15 September 2006; published online 30 October 2006)

Atom probe tomography assisted by femtosecond laser pulses has been performed on a Ni(Pt) film on (100)Si. Two phases with different compositions were found to form during deposition at room temperature: a NiSi layer with a relatively constant thickness of approximately 2 nm and a particle of Ni_2Si. The shape of the Ni_2Si particle is in accordance with nucleation followed by lateral growth formation. This confirms the growth model deduced from calorimetric measurement of silicides and intermetallics and from atom probe tomography studies of the Al/Co system. A nonuniform redistribution of Pt was also observed. © *2006 American Institute of Physics*.
[DOI: 10.1063/1.2370501]

The study of thin film reactions has been mainly developed around silicides due to their application as contacts in microelectronic devices. The reactions in thin films[1] are characterized by a sequential growth, the lack of some equilibrium phases, and sometimes the growth of metastable phases while the simultaneous parabolic growth of all the equilibrium phases is usually observed in bulk interdiffusion couples. Recently, even more complex behavior[2] with the formation of "transient phases" (phases that appear and disappear very rapidly) has been found. Nucleation[3] plays also a crucial role in the formation of some phases (in particular, the silicon rich silicide: $NiSi_2$, $TiSi_2$, etc.). The addition of alloying elements can influence the nucleation of silicides. For example, the addition of 5% Pt to a Ni film increases the temperature of formation of $NiSi_2$ by approximately 150 °C.[4]

For the formation of the first phases it may be argued that nucleation should not be limiting because the driving force should be very large. However, several studies indicate that nucleation is an important and limiting step during the formation of intermetallics. In particular, scanning calorimetry experiments of different systems (Ni/Si,[5] Al/Ti,[6] Al/Co,[7] etc.) have shown that the formation of a unique phase is characterized by two exothermic peaks: the first one corresponds to nucleation and lateral growth, which continues until a continuous layer is formed, while the second one is linked to the thickening of the phase.

Advanced characterization methods with very high spatial resolution are required to analyze the reaction at the nanoscale. Atom probe tomography (APT) has been applied in the analysis of precipitation[8] or thin film formation[9] of nanometric phases. Indeed, atom probe tomography[10] has unique capabilities to characterize internal interfaces and layer chemistry with subnanometer scale resolution in three dimensions. APT has long been limited to materials with good electrical conductivity because fast high voltage pulses were required for field evaporation. However, it has recently been shown that the use of ultrafast laser pulses (<1 ps) enables to analyze specimens with poor conductivity.[11] These innovations in instrumental technology and sample preparation have allowed the characterization of the dopant redistribution in Si[12] and metallic multilayers on Si substrate.[13] Very recently, Thompson *et al.*[14] have reported the observation of the NiSi and Ni_2Si phases after heat treatment at 350 °C for 10 min.

In this letter, we report atom probe observations of the early stages of silicide formation. We produce a direct observation of the nucleation and lateral growth of Ni_2Si at the interface between a phase with a composition close to NiSi and the Ni layer at room temperature.

80 nm thick films of polycrystalline Ni containing 5 at. % Pt were deposited at room temperature by cosputtering of Ni and Pt targets on (100)Si *p*-doped (resistivity of 0.01 Ω cm) substrates. The Ni(Pt) films were deposited simultaneously on (i) blanket substrates for characterization by x-ray diffraction (XRD) and x-ray reflectivity (XRR) and on (ii) high aspect ratio flattopped ⟨100⟩ silicon posts for the atom probe tomography analyzis. In the APT technique, a tip is evaporated atomic layer by atomic layer and analyzed by time-of-flight mass spectrometry, allowing a small volume of material (typically $15\times15\times100\ nm^3$) to be reconstructed in the three dimensions of space, atom by atom on a nearly atomic scale.[10] For this study, the region of interest was transformed[15] into a tip with a 30 keV Ga^+ focused ion beam system. XRD and XRR were performed using the Bragg-Brentano geometry and a Cu $K\alpha$ source. The atom probe

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0003-6951/2006/89(18)/181905/3/$23.00

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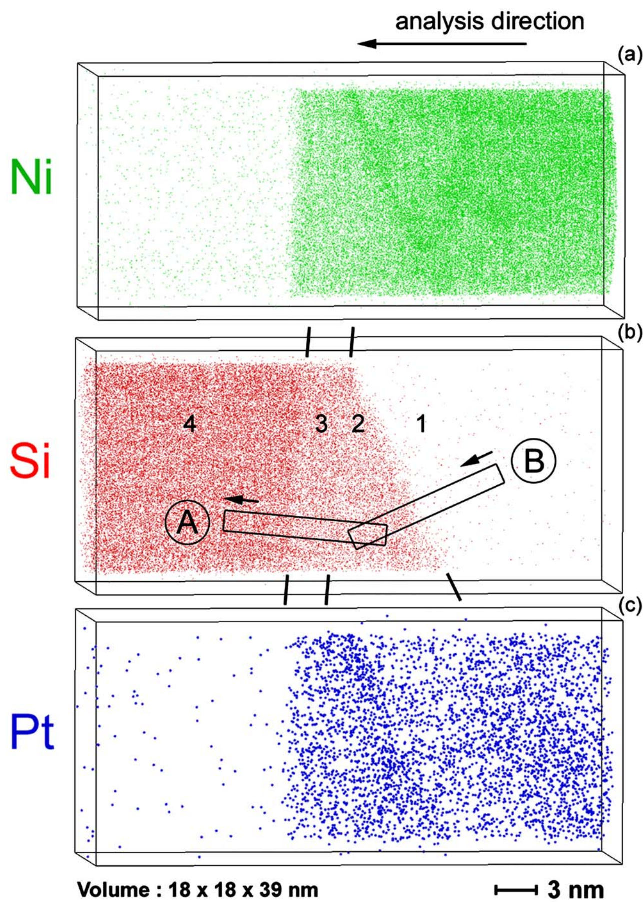

FIG. 1. (Color online) 3D images an obtained from the laser assisted TAP analysis of a Ni-5%Pt film on (100)Si without heat treatment for (a) Ni, (b) Si, and (c) Pt with schematic of sampling boxes A (volume of $1\times1\times8$ nm) and B (volume of $1\times1\times8$ nm).

tomography characterization was performed using the laser assisted tomographic atom probe (LATAP). The laser system is an amplified ytterbium doped laser (Amplitude System *s* pulse, $\lambda=1030$ nm). Analyses were performed using an ~6 μJ/350 fs pulse focused onto an ~0.1 mm^2 spot.

Figure 1 shows the APT reconstructions of the as-deposited sample. The reconstructed volumes were oriented in order to image the interfaces perpendicular to the plane of view. From the Ni distribution [Fig. 1(a)] and Si distribution [Fig. 1(b)] four different regions are detected: a region with almost no Ni corresponding to the Si substrate (region 4), a region with almost no Si corresponding to the metal layer (region 1), and two regions containing both Ni and Si (regions 2 and 3).

In order to determine the composition of these regions, two sampling boxes A and B were used [Fig. 1(b)]. Several ways of determining the compositions were tried and it was found that the use of integral concentration give the most precise determination (Fig. 2). The slope of these curves gives the atomic fraction. Regions 1–4 were identified, respectively, with slopes of 0.01, 0.31, 0.45, and 0.97 for Si and with slopes 0.96, 0.63, 0.50, and 0.03 for Ni leading to a composition close to NiSi for region (3) and to Ni_2Si for region (2). The redistribution of Pt in the sample is relatively complex and follows neither the Ni nor the Si.

In order to estimate the shape of regions 2 and 3, the local Si concentrations were measured within a sampling box of 8 nm^3 and compared with two different ranges: (i) 47%–

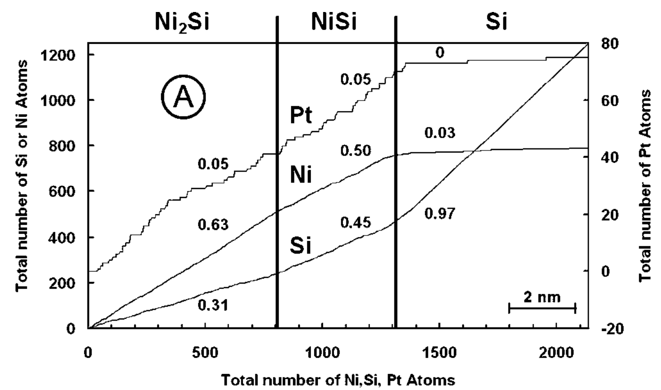

FIG. 2. Integral concentration profiles: cumulated number of Ni, Si, and Pt as a function of the total cumulated number of atoms for sampling box A. The slopes of the curve are indicated and give the concentration.

53% and (ii) 30%–36%. The corresponding volumes were then reconstructed for the first [Fig. 3(a)] and second [Fig. 3(b)] ranges. Figure 3 shows that region 3 (NiSi) has a relatively constant thickness of about 2 nm while region 2 (Ni_2Si) has a shape of a part of a cut lens. One can see in Fig. 3(c) that there might be another layer between Ni and Ni_2Si. However, it was not possible to clearly determine the composition and thickness of this layer.

To obtain complementary information, XRR and XRD measurements (not shown here) were performed on the thin film as-deposited sample. The XRR spectrum clearly indicates two types of oscillation that correspond to the Ni layer and to a layer with a thickness of about 2 nm. An XRD experiment with a large statistic (12 h counting time) did not reveal any XRD peaks other than the ones of Ni and Si.

The present results indicate that after deposition of a Ni-5%Pt film at room temperature, two silicides are present: a roughly constant thickness layer with a composition close to NiSi and a cluster with a composition close to Ni_2Si. The

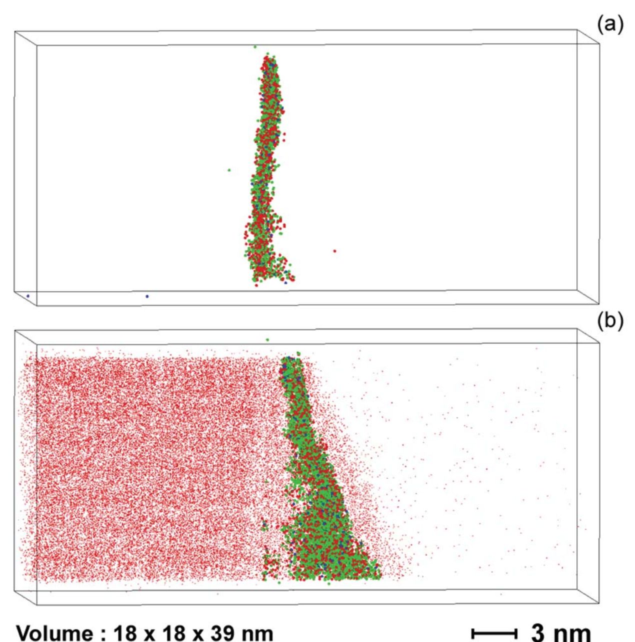

FIG. 3. (Color online) Reconstructed volume with a concentration of Si within a sampling box of 8 nm^3 comprised between (a) 47%–53% and (b) 30%–36% with all the Si atoms are drawn.

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XRD and XRR results seem to indicate that an amorphous phase is formed during deposition of the metal alloy as reported in several cases,[16,17] including Ni/Si.

Our XRD results did not reveal the presence of Ni_2Si. We reject a local heating of the tip during the sample preparation and/or the APT analysis. Indeed the temperature rise during focused ion beam milling is estimated to only be on the order of 10 °C and, very recently,[18] the maximum temperature during LATAP investigations has been measured to be less than 160 K just after laser pulses and to decrease in a few hundreds of nanoseconds down to the usual investigation temperature (70 K). The absence of an XRD peak related to Ni_2Si is certainly due to the detection limit.

At first glance, one might think that the Ni_2Si particle corresponds to a nucleus of Ni_2Si. However, the size of the Ni_2Si particle is relatively large as compared to the typical critical size of a nucleus. Indeed the formation of a critical nucleus requires fluctuations in composition[19,20] and this should limit the critical size to a few nm^3. An estimate with typical Gibbs free energies (a few tens of kJ/mol) and typical interface energies (a few hundreds of mJ/m^2) gives also a few nm^3. In the present case, the interface energies and driving force are not known and it is not possible to give the critical size for nucleation. Some difficulties in nucleation may have been expected due to the formation of the first phase (with the composition close to NiSi). Indeed the formation of this phase should reduce the driving force for the formation of Ni_2Si.[3] The sharp gradient of concentration may also limit the nucleation.[21,22] However, the presence of Ni_2Si at room temperature indicates that the nucleation certainly occurs during deposition. During the deposition, the situation is quite different than during solid state reaction.[23] The situation observed in Fig. 2 is thus certainly not the first stage of nucleation but a later stage where the growth of the nucleus has already started. Our results provide a direct observation and give evidence that the formation of nickel silicides, and certainly of silicides in general, starts by nucleation and lateral growth. Our results are in accordance with the calorimetric studies of reactive diffusion in thin films: these studies have demonstrated that the formation of the first product often proceeds via two well distinct steps (two calorimetric peaks), starting by nucleation and lateral growth along the interface and followed by a growth in the normal direction.[4] The quantitative evaluation of the differential scanning calorimetry peak corresponding to nucleation and lateral growth usually gives a thickness of the first layer of about 10 nm, a value significantly larger than the critical size of a nucleus. Vovk *et al.*[9] have also found, by APT investigations of Al/Co bilayers, particle and layers after the first step with thickness ranging from about 5 to 15 nm. Following Klinger *et al.*[24] and Lusenko and Gusak,[25] they have proposed a model of growth where the minority elements diffuse along the interphase boundaries and allow the growth of the intermetallic without diffusion in the growing phase. According to these models the precipitates can grow well above the critical nucleus size before forming a continuous layer. These models can also explain the nonsymmetrical shape of the growing phase observed in the Al/Co system and in our work for Ni_2Si (Fig. 3). This shape should be due to an anisotropy of diffusion at the interphases: in the Al/Co system, the intermetallic particles were always on the Al side of the interface and this was explained by faster growth at the Al_9Co_2/Al interface. It seems that the Ni(Pt)/Si system behaves relatively similarly to the Al/Co system since the Ni_2Si particle is much more developed at the Ni_2Si/Ni interface.

To conclude, the early stage of silicide formation was investigated by laser assisted atom probe tomography of an Ni (5% Pt) film on (100)Si without heat treatment. It has been shown that

(1) the formation of silicide begins during deposition,
(2) two regions with composition corresponding to NiSi and Ni_2Si are present,
(3) while NiSi forms a film with a relatively constant thickness, the shape of the Ni_2Si particle is in accordance with a nucleation and growth process by diffusion along the interphase boundary (This is a direct evidence that the formation of silicides starts by nucleation and lateral growth and confirms the former results obtained by calorimetry.), and
(4) the Pt redistribution has been measured at the nanometric scale and is relatively complex.

The authors would like to thank David J. Larson for providing the Si posts. Discussions with Claire Bergman are greatly acknowledged. One of the authors (D.M.) would like to dedicate this work to Patrick Gas who left them in 2005.

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