JOURNAL OF MATERIALS SCIENCE 30 (1995) 3242–3247

Cu–Ni and Ni–Cu bilayers on silicon: reduction of formation temperature and phase separation

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The solid state reaction between Ni–Cu and Cu–Ni bilayers on Si(1 0 0) has been studied using X-ray diffraction, transmission electron microscopy, Auger electron spectroscopy and sheet resistance measurements. The bilayers were produced by evaporation and annealed at temperatures between 200 and 500 °C. In the Ni–Cu sequence, a strong intermixing of silicides and a 33% reduction in the formation temperature of the $NiSi_2$ phase compared with Ni–Si(1 0 0) was observed. When nickel was in direct contact with the silicon substrate limited intermixing and reaction of Cu was observed in the Cu–NiSi and NiSi–Si interfaces at 500 °C, due to the large grain size of the nickel silicide.

1. Introduction

Thin film interactions for ternary metal–metal–silicon systems are of great interest in two contexts: they form a shallow silicide contact due to the miniaturization of very large scale integrated (VLSI) electronic devices in VLSI technology [1], and they allow a better understanding of metallurgical aspects, such as phase separation, ternary silicide formation and solid solution of silicides [2].

Recently, much attention has been focused on Cu silicide, because copper is an interconnection material for VLSI circuits [3, 4]. Many aspects of Cu interaction in metallic bilayers deposited onto silicon were also studied. For example, phase separation of Co–Cu bilayers [5], ternary silicide formation of $Nb_5Cu_4Si_4$ in Nb–Cu bilayers [6], and reduction in the formation temperature of Re silicide in Re–Cu bilayers [7] have been reported. Nickel–metal bilayers on silicon, on the other hand, can form ternary silicides, such as $Ti_4Ni_4Si_7$ in Ti–Ni [8] and $Nb_4Ni_4Si_7$ in Nb–Ni [9] bilayers; pseudobinary solid solution of Co–Ni bilayers can occur with a reduction in the formation temperature of the $NiSi_2$ phase [10], and can produce phase separation as in the case of Cr–Ni bilayers, which exhibit layer sequence reversal [11]. However, the separate behaviour of copper and nickel with silicon is fairly well known, but interaction of these two metals with silicon is little known. Bai *et al.* [12] have reported the formation of a complete solid solution in one Ni–Cu bilayer deposited on Cr–ceramic and annealed at 350 °C for 30 min. In bilayers of Ni–Cu–Si, Chang [13] showed the existence of Cu silicides at 200 °C and Ni silicides at 300 °C. Similar results were found for the Cu–Ni–Cu–Si structure [14].

This paper presents the phase evolution studies versus annealing temperature of Ni–Cu and Cu–Ni bilayers deposited onto silicon. The main metallurgical aspects are the formation temperature of the silicides and the growth of different phases.

2. Experimental procedure

Metallic bilayer thin films were deposited on *n*-doped Si(1 0 0), 5–8 Ω cm, wafers which were prepared using a standard chemical cleaning procedure [3]. The wafers were then loaded into an evaporator with a base pressure prior to deposition of 1.3×10^{-4} Pa. Films with thicknesses of 240 nm of nickel and 200 nm of copper were sequentially deposited onto Si(1 0 0) substrates, without opening the vacuum chamber. The deposition rate was kept constant for both copper and nickel films ($0.3\ nm\ s^{-1}$). The substrate temperature was held below 50 °C during deposition. The thicknesses of bilayers were measured by a Sloan Dektak II. Slices of the samples of about 1 cm^2 were submitted to individual heat treatment for 30 min at temperatures of 200, 300, 400 and 500 °C. The annealing was performed in a quartz tube furnace pumped by a turbomolecular pump. The pressure during the annealing process was better than 6.67×10^{-5} Pa.

Complete elemental analysis of samples as a function of depth was performed with Auger electron scanning (AES). AES depth profiling was carried out in a PHI SAM 590 microprobe using a primary electron beam at 3 keV, 2 nA, while the surface was sputter etched with a 2 keV argon ion beam. A standard Rigaku powder diffractometer was used for X-ray diffraction (XRD) measurements with molybdenum radiation for phase identification, and sheet resistance measurements were used to follow the behaviour of bilayers with annealing temperature. A Jeol JEM 2000 FX transmission electron microscope (TEM) was used to investigate the grain size of the phases in evolution. In sample preparation for TEM, the silicon substrate was etched chemically from the

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backside with a HF:HNO_3 solution to permit electron transmission.

3. Results

3.1. Cu–Ni–Si(1 0 0) system

Table I summarizes all the data obtained with XRD and TEM. Fig. 1 shows the TEM image together with the corresponding diffraction pattern for the as-deposited sample. A polycrystalline structure is observed, with grain sizes of about 10 nm. The observed rings in the diffraction pattern were referenced to nickel and copper with a diversity of orientations. The AES depth profile of the as-deposited sample, shown in Fig. 2a, reveals that both the Ni–Si and Cu–Ni interfaces show some intermixing, though no phase has been observed. After annealing at 200 °C, XRD reveals the presence of a small peak of Ni_2Si.

At 300 °C, XRD reveals a more accentuated consumption of the Ni layer. From the TEM image presented in Fig. 3 it is possible to observe a complex morphology. The diffraction pattern presents, along with Cu, Ni and Ni_2Si rings, some other rings which could be referenced to Cu_3Si and Cu_4Si. After annealing at 400 °C, XRD shows an unusual coexistence of Ni, with the Ni_2Si and NiSi phases.

At 500 °C the reaction of nickel is complete, as can be seen in the AES depth profile presented in Fig. 2b. The AES profile reveals that some copper remains unreacted. This is confirmed by XRD (not shown), which reveals the presence of a small peak of Cu(1 1 1). From the TEM image presented in Fig. 4, it is possible to observe an increase in grain size of NiSi from over 17 to 95 nm. The growth of NiSi grains is confirmed by XRD between 400 and 500 °C. At these temperatures occurs the formation of the Cu–(Cu_3Si + Cu_4Si + NiSi)–NiSi–Si(1 0 0) structure.

The sheet resistance measurements are shown in Fig. 5. It is seen that the Cu–Ni–Si(1 0 0) structure shows the smallest change in sheet resistance with annealing temperature up to 300 °C. At 400 °C a small resistance rise is observed, which is connected with the growth of Ni_2Si and the formation of an NiSi phase. The drop at 500 °C is attributed to an increase in the grain size of NiSi.

TABLE I Phases identified by X-ray diffraction and electron diffraction as a function of annealing temperature for Cu–Ni–Si(1 0 0) and Ni–Cu–Si(1 0 0) systems

Annealing temperature (°C)	Cu–Ni–Si(1 0 0)	Ni–Cu–Si(1 0 0)
As-deposited	Cu, Ni	Ni, Cu
200	Cu, Ni, Ni_2Si	Ni, Cu, Cu_3Si, Cu_4Si
300	Cu, Ni, Ni_2Si, Cu_3Si, Cu_4Si	Ni, Cu_3Si, Cu_4Si
400	Cu, Ni, Ni_2Si, NiSi, Cu_3Si, Cu_4Si	Ni, Ni_2Si, NiSi, Cu_3Si, Cu_4Si
500	Cu, NiSi, Cu_3Si, Cu_4Si	$NiSi_2$, NiSi, Cu_3Si, Cu_4Si

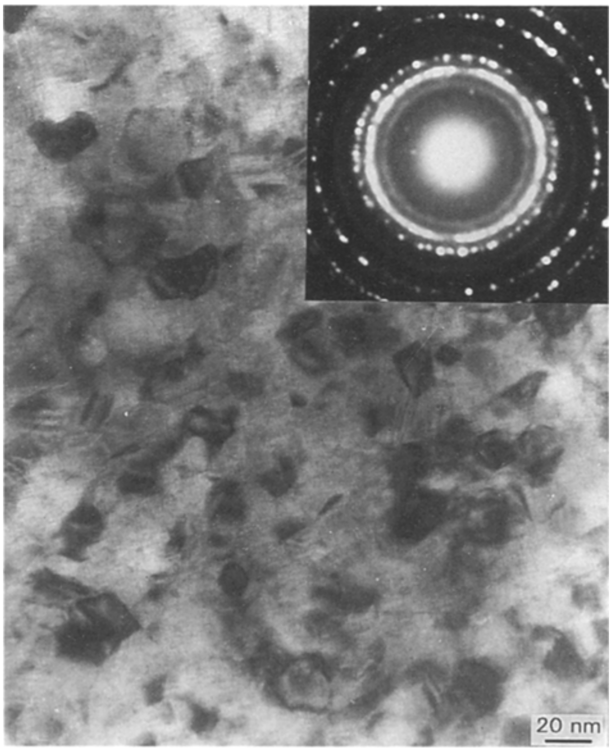

Figure 1 TEM micrograph of a plane view specimen made from the Cu–Ni–Si(1 0 0) as-deposited sample.

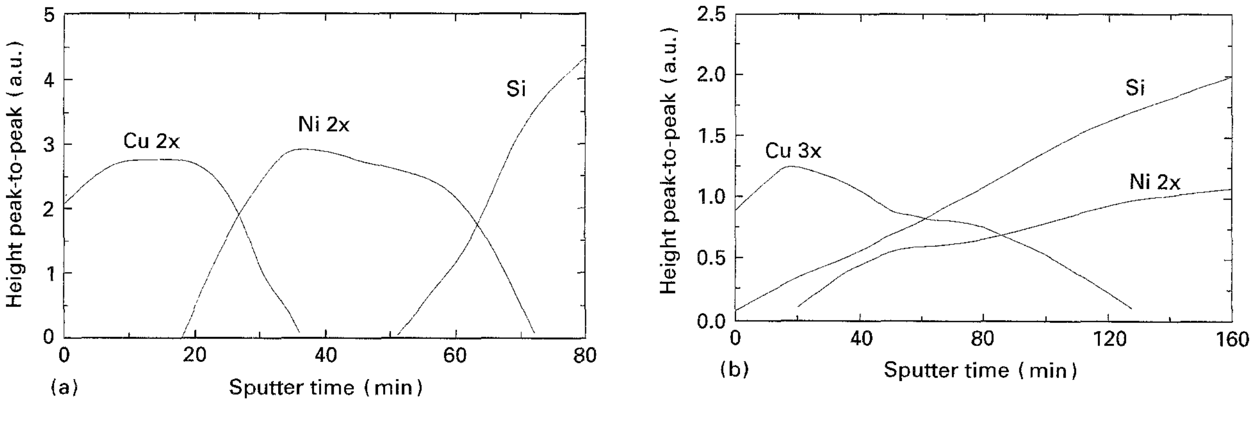

Figure 2 AES depth profiles of the Cu–Ni–Si(1 0 0) sample at room temperature (a) and annealed at 500 °C for 30 min (b).

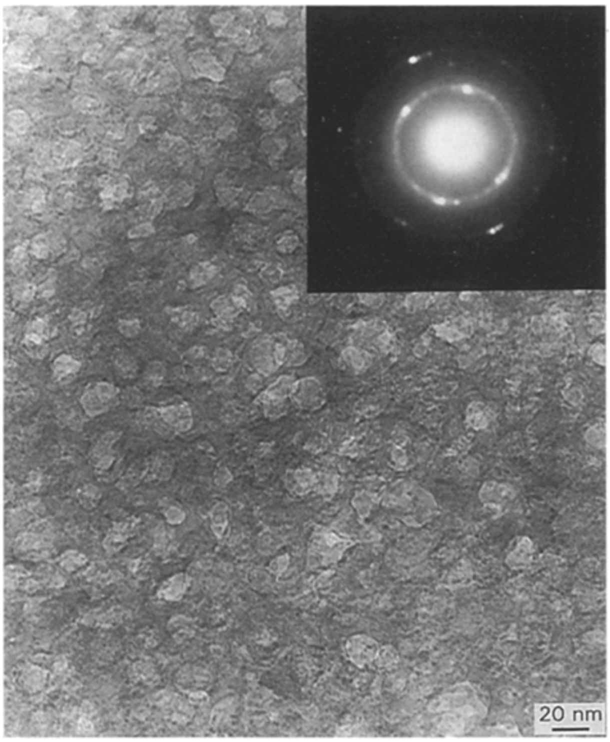

Figure 3 TEM bright field image and select area diffraction results obtained from a sample of Cu–Ni–Si(1 0 0) annealed for 30 min at 300 °C.

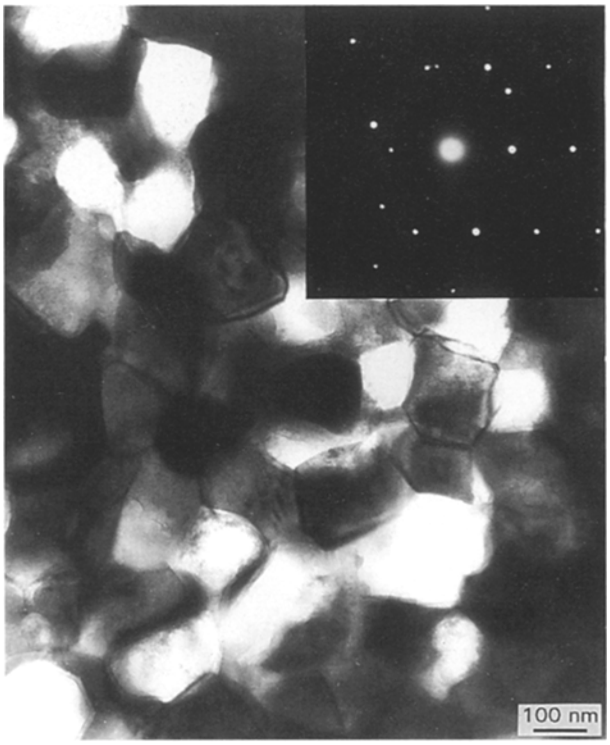

Figure 4 As in Fig. 3, for Cu–Ni–Si(1 0 0) annealed for 30 min at 500 °C.

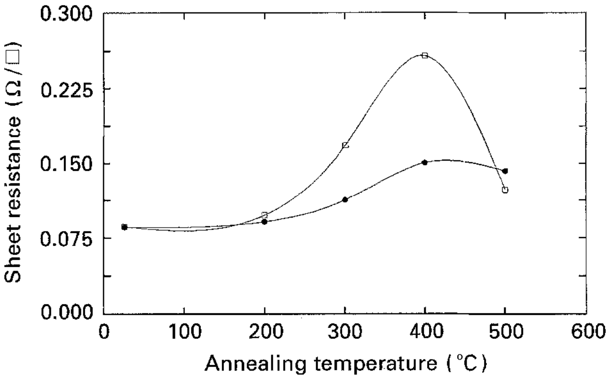

Figure 5 Influence of annealing temperature on the sheet resistance of (●) Cu–Ni–Si(1 0 0) and (□) Ni–Cu–Si(1 0 0) bilayers.

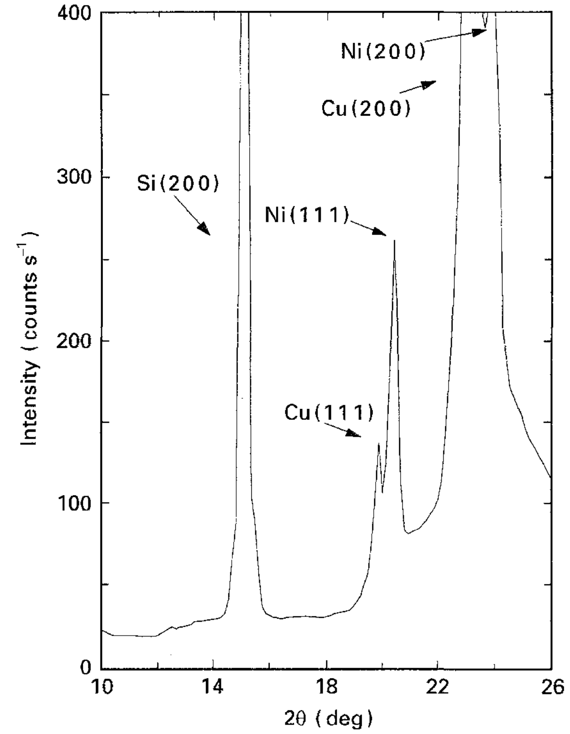

Figure 6 X-ray diffraction pattern of Ni–Cu–Si(1 0 0) structure, showing mainly the (2 0 0) preferred orientation of Ni and Cu layers.

3.2. Ni–Cu–Si(1 0 0) system

When copper is the first layer deposited on the silicon substrate, a texture in both Ni and Cu films along the ⟨1 0 0⟩ orientation is observed, as can be seen in the X-ray spectrum presented in Fig. 6. The AES profile, presented in Fig. 7a, shows no intermixing, neither at the Cu–Si nor at the Ni–Cu interfaces. After annealing at 200 °C, XRD reveals the presence of Cu_3Si and Cu_4Si.

At 300 °C, the copper layer was totally reacted. XRD presents, in addition to the Cu_3Si, Cu_4Si and nickel peaks, some other peaks which could be identified as Ni_2Si. This is confirmed by the electron diffraction pattern in TEM (see Fig. 8). The TEM image presents grains of a copper silicide, with a grain size of about 4 nm, in coexistence with Ni grains. At 400 °C, the X-ray spectrum reveals that almost all the Ni film was reacted and that the same unusual coexistence of Ni, Ni_2Si and NiSi phases appeared.

The AES profile for the sample annealed at 500 °C presented in Fig. 7b, reveals strong interdiffusion between Ni–Cu–Si in the copper silicide layer, and the existence of two layers of nickel silicides. From XRD shown in Fig. 9, it is possible to identify the Cu_3Si, Cu_4Si, NiSi and $NiSi_2$ phases and the hunch formed

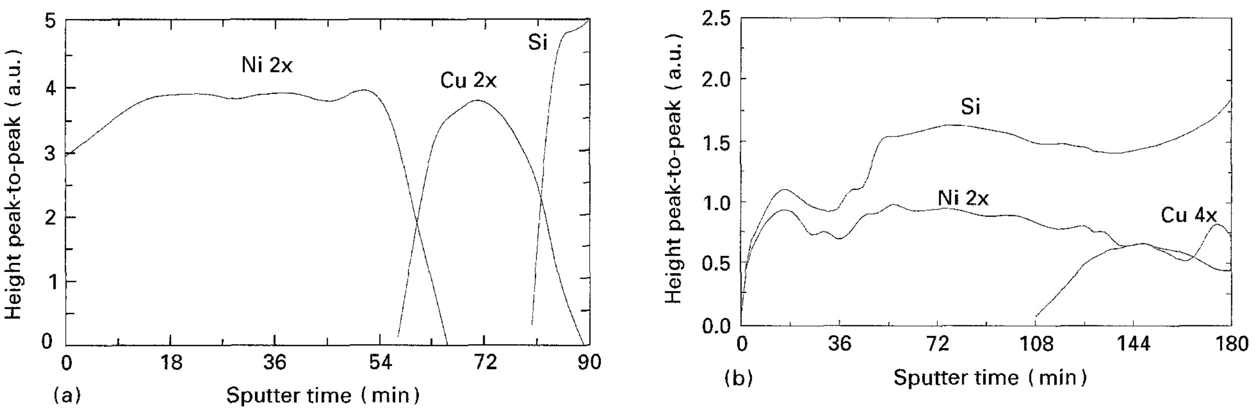

Figure 7 AES depth profile of Ni–Cu–Si(1 0 0) sequence: (a) room temperature and (b) annealed for 30 min at 500 °C.

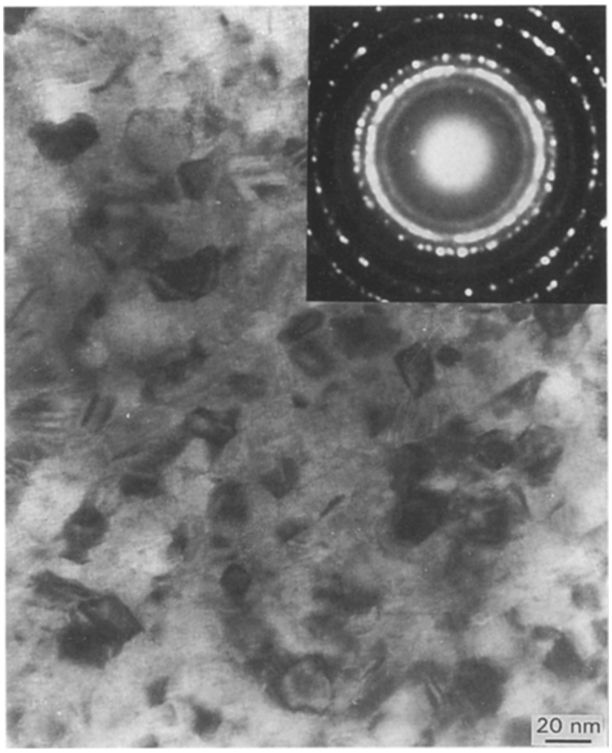

Figure 8 TEM micrograph results obtained from a sample of Ni–Cu–Si(1 0 0) annealed for 30 min at 300 °C.

by the amorphous reaction region. According to the AES profile presented in Fig. 7b, the structure formed is NiSi–($NiSi_2$ + Cu_3Si + Cu_4Si)–Si(1 0 0).

Fig. 5 shows the sheet resistance versus annealing temperature for sequence Ni–Cu–Si(1 0 0). The increase of the resistance from 200 to 300 °C, is associated with the formation of Cu and Ni silicides, respectively. The large increase in the sheet resistance at 400 °C is attributed to NiSi formation in coexistence with other silicides. The decrease in the sheet resistance at 500 °C is attributed to the $NiSi_2$ phase formation (see Fig. 9). This phase has a lower resistivity in comparison with the NiSi phase [15].

4. Discussion

Silicide formation in Ni films grown on silicon has been extensively studied [16]. The reaction of nickel

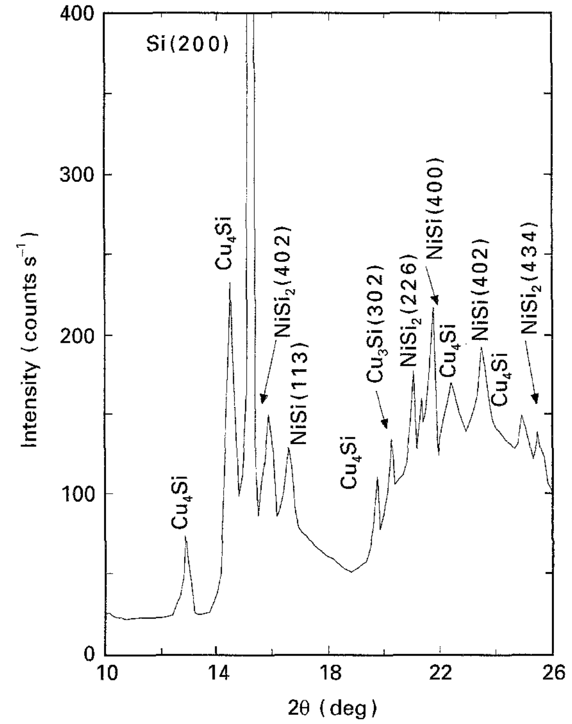

Figure 9 X-ray diffraction pattern showing the formation of both Cu and Ni silicides in Ni–Cu–Si(1 0 0) structure annealed at 500 °C for 30 min.

with silicon results in the formation of Ni_2Si at 200 °C, NiSi at 350 °C and $NiSi_2$ at $\leqslant 750$ °C [17]. Four copper silicide phases are stable at room temperature [18], γ-Cu_5Si, ε-$Cu_{15}Si_4$, Cu_4Si and η″-Cu_3Si. This later results in direct reaction of copper with silicon substrate at 200 °C [19]. The Cu–Ni system has no phases predicted by the phase diagram [20].

In the Cu–Ni–Si sequence both Cu–Ni and Ni–Si interfaces show a little intermixing, but XRD and TEM reveal no signals of silicides formation, indicating that no reaction has occurred during the deposition process in the as-deposited sample. However, at 200 °C one can observe the small reaction of the nickel film for the sample annealed, resulting in the formation of an Ni_2Si phase in accordance with Ottaviani [17].

The interdiffusion process in the Cu–Ni interface is confirmed through the presence of the Ni_2Si, Cu_3Si and Cu_4Si shown in the TEM image and electron diffraction pattern for the sample annealed at 300 °C. At 400 °C almost all the nickel film is reacted resulting in the formation of an unusual coexistence of Ni, Ni_2Si and NiSi. This fact was first reported by Olowolafe et al. [16] in the Ni–*a*-Si system. Generally, only one phase is observed each time in reactions of metal films with silicon [17]. In spite of this, Zhang and Ivey [21] reported that the phase formation and growth kinetics are determined by thermodynamic factors and by flux of diffusing element; indicating that these results can be produced by copper silicide at the Ni–Si interface, as in case of the Cu–Nb–Si(1 0 0) system [6].

At 500 °C some copper remains unreacted (see Fig. 2b) indicating limited intermixing and reaction at the Cu–NiSi interface. This fact can be explained by the greater grain size of the NiSi phase, which has increased around 460% (400–500 °C). The smaller boundary region probably reduces diffusion and reaction of the copper layer.

In the Ni–Cu–Si structure a strong texture is observed in the ⟨1 0 0⟩ orientation (see Fig. 6) in the as-deposited sample. Chang *et al.* [22] have reported epitaxial growth of the Cu(1 0 0) on Si(1 0 0) through a 45° rotation of the Cu(1 0 0) lattice relative to its ⟨0 0 1⟩ axis, which reduces the mismatch of Cu–Si from over 40 to 6%. The epitaxial growth of the Ni films on epitaxial Cu film has been reported by Chang [13] with a large deposition rate ($1\ nm\,s^{-1}$). These results, in addition with the results presented in this work, show evidence of the importance of deposition rate in epitaxial growth of Cu films on silicon substrates. The effect of rate deposition in thin films on epitaxial growth has been reported by Murr [23], who related this effect for epitaxial growth of palladium films on NaCl substrates. For annealed samples one can observe a large consumption of the Cu film, resulting in the formation of the Cu_3Si and Cu_4Si phases at 200 °C.

When the silicon is in contact with nickel, Ni_2Si is the first phase to be formed at 300 °C. In this system exists a large reactivity, probably due to a large flux of silicon through large boundary regions of copper silicide, as can be seen in Fig. 8. With the increase of temperature, a large quantity of reactive silicon atoms reach the reaction region with nickel. In consequence, phases richer in silicon start to grow. This is confirmed by the sample annealed at 400 °C. At this temperature occurs the same unusual coexistence of Ni, Ni_2Si and NiSi.

After annealing at 500 °C, an unexpected $NiSi_2$ phase is observed by XRD (see Fig. 9). At this temperature the flux of the silicon atoms is much larger and this solid state interdiffusion process probably creates favourable conditions to promote the formation of $NiSi_2$. The sheet resistance measurements are in agreement with this fact. Another important result is that copper silicide has catalytic effects on the growth of SiO_2 [24]. This fact could contribute to a reduction in the formation temperature of the $NiSi_2$ phase. A similar case was observed by Ronay and Schad [7]. They reported the reduction in formation temperature of $ReSi_2$ from over 900 to 550 °C in Re–Cu–Si(1 0 0) and Cu–Re–Si(1 0 0) systems. According to these authors, reduction of the formation temperature of the $ReSi_2$ phase occurs due to the existence of silicon atoms released from the silicon matrix, because copper atoms occupy interstitial positions around a silicon atom and force the central silicon atom out of position.

In both cases, reduction in the formation temperature is strongly affected by the flux of silicon atoms reaching the reaction region. This is possible, in the case of copper silicide, because the copper silicide formation process increases the quantity of free silicon atoms available for reaction. Together with this fact, copper silicide has large boundary regions, which permit a greater flux of silicon atoms, favouring the growth of silicides at lower temperatures. Therefore, the model of Zhang and Ivey [21] is very important in understanding the reduction of formation temperature of silicides. They affirm that only those reactions that are thermodynamically allowed and kinetically preferred can occur, and that kinetic preference is determined by composition in the reaction region, which is controlled by the diffusion flux of the moving reactant. In this case, the flux of silicon atoms.

5. Conclusions

The interaction of thin films of Cu–Ni bilayers with Si has been studied by different analytical techniques, namely AES, XRD, TEM and sheet resistance measurements. The results indicate that in the sequence Cu–Ni–Si(1 0 0) an unusual coexistence of phases (Ni, Ni_2Si and NiSi) at 400 °C can be observed. At 500 °C, the large grain size of NiSi impedes complete consumption of the copper film. The Ni–Cu–Si(1 0 0) sequence exhibits the same unusual coexistence of phases at 400 °C, and the small grain size of copper silicide eases the reduction in the formation temperature of $NiSi_2$ phase from over 750 to 500 °C. In both systems a large intermixing layer can be observed.

Acknowledgements

The author would like to thank Dr Carlos A. Achete, Universidade Federal do Rio de Janeiro, for assistance in experimental work and Dr Dante H. Mosca Jr for critical review of the manuscript. This work was supported partially by CAPES and CNPq, Brazilian research sponsoring agencies.

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Received 3 December 1993
and accepted 25 November 1994