Simultaneous planar growth of amorphous and crystalline Ni silicides

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We report a solid-state interdiffusion reaction induced by rapid thermal annealing and vacuum furnace annealing in evaporated Ni/Si bilayers. Upon heat treatment of a Ni film overlaid on a film of amorphous Si evaporated from a graphite crucible, amorphous and crystalline silicide layers grow uniformly side by side as revealed by cross-sectional transmission electron microscopy and backscattering spectrometry. This phenomenon contrasts with the silicide formation behavior previously observed in the Ni-Si system, and constitutes an interesting counterpart of the solid-state interdiffusion-induced amorphization in Ni/Zr thin-film diffusion couples. Carbon impurity contained in the amorphous Si film stabilizes the amorphous phase. Kinetic and thermodynamic factors that account for the experimental findings are discussed.

The phase evolution of silicides in metal/Si thin-film diffusion couples has been a subject of continuing interest for many years.[1,2] It has been well established that typically only one of the equilibrium silicides predicted by the phase diagram grows until either metal or silicon is fully consumed.[2] The absence of the other silicides expected to appear in bulk diffusion couples has been attributed to the presence of a nucleation barrier[3,4] and/or to the kinetic instability imposed by interface reaction barriers in thin films.[4,5] Recent investigations of solid-state interdiffusion reactions in metal/metal thin-film couples have shown that the formation of the first crystalline intermetallic compound is often preceded by the planar growth of an amorphous phase to a considerable thickness (e.g., more than 100 nm).[6] The prerequisites for such an amorphization are (i) a large negative heat of mixing in the binary system and (ii) the dominant fast atomic transport of one of the constituent species (fast diffuser) in the other (matrix). These criteria are also met in some metal/Si systems, e.g., the Ni/Si system where the dominant moving species, Ni, is a fast diffuser in Si and nickel silicides.[2,7] Although amorphous silicide phases have been observed in a number of metal/Si systems,[8–15] large-scale amorphous phase growth (e.g., to a few hundred angstroms thick) by low-temperature interdiffusion is rarely seen. In the case of Ni-Si, it is found in a recent electron microscopy study of the initial stage of silicide formation in very thin evaporated Ni/amorphous-Si films that an amorphous Ni-Si phase is present after deposition of a few nm Ni. The amorphous phase, however, is very unstable and soon is taken over by crystalline silicides as an increasing amount of Ni is deposited at room temperature.[15] Apparently it is the intrinsic ease of crystalline silicide formation in this system at low temperatures that precludes any appreciable growth of an amorphous phase by solid-state interdiffusion. A change in sample conditions, e.g., the addition of impurities, may significantly influence the phase competition and evolution. In this letter, we describe the reaction outcome in Ni/*a*-Si bilayers as deposition conditions for Si are varied.

Bilayered Ni/*a*-Si films were prepared by sequential electron beam evaporation onto a (100)Si substrate in the configuration (100)Si/ ~ 150–200 nm Si/ ~ 200–250 nm Ni. Two types of samples have been produced in two oil-free evaporation units with a base pressure of about 5×10^{-8} Torr. The vacuum during the evaporation of all the samples was kept below 3×10^{-7} Torr. For the first sample set (hereafter referred to as type *A*), evaporations of Si and Ni were executed directly from water-cooled copper hearths, whereas for the other set of samples (hereafter referred to as type *B*), a graphite crucible was inserted in the copper hearth to contain the Si, but not in the Ni hearth. Auger electron spectroscopy (AES) measurements show that the carbon content is below the detection limit (~ 1 at. %) in type *A* samples, but is distributed fairly uniformly at a concentration on the order of ~ 7 at. % in the amorphous Si layer of type *B* samples. Such appreciable amount of carbon is seen in type *B* samples prepared separately in both evaporation units. A 2.27 eV shift of the C 1*s* binding energy shown by x-ray photoelectron spectroscopy suggests that carbon probably is locally bonded to Si. Oxygen is not detectable by AES in either type of samples. Thermal annealing was carried out in a furnace with a vacuum of $\sim5\times10^{-7}$ Torr at temperatures from 240 to 300 °C. Some samples were processed by rapid thermal annealing (RTA) in ultrapure argon (99.999%) at 350 °C, a temperature which is only nominal due to a large uncertainty in absolute temperature measurement for short annealing durations.[16] Analysis was performed with cross-sectional transmission electron microscopy (XTEM) and 2.0 MeV $^4He^+$ backscattering spectrometry (BS).

Furnace annealing of type *A* samples yields the columnar growth of a single Ni_2Si phase having a growth kinetics consistent with previous reports.[2,17,18] However, very different results are obtained from type *B* samples under the same furnace annealing conditions, as well as for RTA treatments. We will use *A*-type samples for comparison purposes only and concentrate on the carbon-containing *B*-type samples in the rest of this letter.

A series of BS spectra for type *B* samples after RTA at 350 °C for different durations is presented in Fig. 1. The corresponding XTEM bright-field micrographs for these samples are shown in Fig. 2. The stepped structure exhibited in

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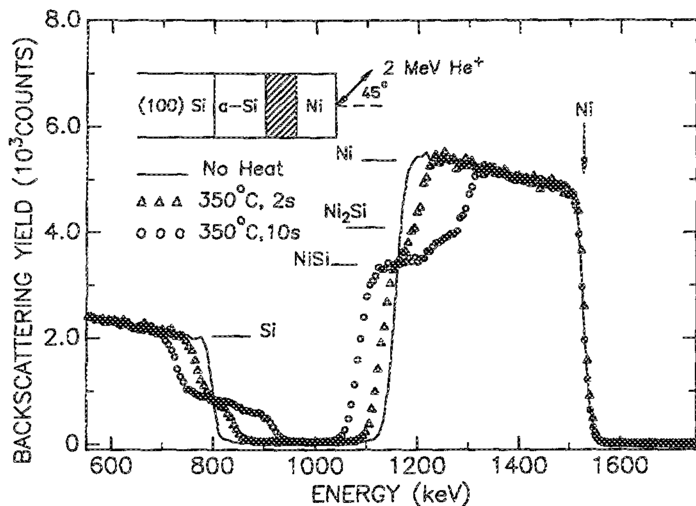

FIG. 1. Backscattering spectra of type B samples as-deposited and rapid thermally annealed at a nominal 350 °C for 2 and 10 s. The 2 MeV $^4He^+$ beam is incident at 45° from the sample normal and the scattering angle is 170°.

the BS spectra is entirely different from those for type A samples where only a single plateau corresponding to Ni_2Si develops. The growth of two phases in distinct layers with sharp interfaces is clearly seen in the XTEM pictures. The striking feature of these micrographs is the formation of a thick amorphous layer in addition to a layer largely composed of columns of crystalline silicide. The compositions of these phases and their evolution are provided by BS analysis. After annealing for 2 s at 350 °C, a Ni concentration gradient of ~17 at. % is present across the two thin interlayers (the two layers are not yet well resolved in the BS spectra). This total Ni concentration drop remains unchanged after further annealing to 10 s. The much better developed steps in the RBS spectra reveal a Ni concentration gradient of about 6 at. % in each individual layer and a discontinuity of roughly 5 at. % at the interface between these two layers. The composition of the crystalline layer is about 64 at. % Ni, which is close to that of Ni_2Si, normally the first silicide formed in this system. This phase has also been confirmed by glancing angle x-ray diffraction (Read camera) analysis. The amorphous phase, on the other hand, possesses a composition of about 50 at. % Ni, which is close to the lowest eutectic of the system.[19] AES analysis after reaction reveals that the carbon originally in the unreacted Si is retained in the silicide layers without much redistribution during silicide growth. The data of silicide thickness extracted from the XTEM micrographs for samples treated in the furnace at 240 °C and by RTA at 350 °C indicate a $t^{1/2}$ dependence, and hence a diffusion-controlled growth of both layers, with the amorphous phase having a larger apparent growth rate than its crystalline counterpart. The growth of the overall reacted region composed of these two layers is slightly faster than that of a single Ni_2Si phase at the same temperatures in our type A samples. Using the experimental growth rates and the Ni concentration gradients across the layers and assuming that Ni is the dominant moving species, we can estimate the diffusivity of Ni in each of the two layers during the multiphase growth.[4,5,20] The values we found at 240 °C are on the order of 10^{-14} cm^2/s for both layers. Similar magnitude is reached for Ni diffusion during the growth of the amorphous Ni-Zr phase by thermal interdiffusion at temperatures above 300 °C.[6,21–23] It is worth pointing out that the simultaneous planar growth of the two phases has been consistently reproduced in three groups of separately prepared type B samples by either RTA or conventional vacuum furnace annealing.

Barring impurity effects, the growth of an appreciable amorphous layer in a Ni/Si bilayered diffusion couple, as in many metal/metal couples, appears to have been bypassed due to the intrinsic ease of crystalline silicide formation even at room temperature.[15] According to the kinetic model for multiphase growth in thin films outlined by Gösele and Tu,[5] an amorphous phase, if it nucleates at all, may shrink away as it is consumed by the competing crystalline phase. In our

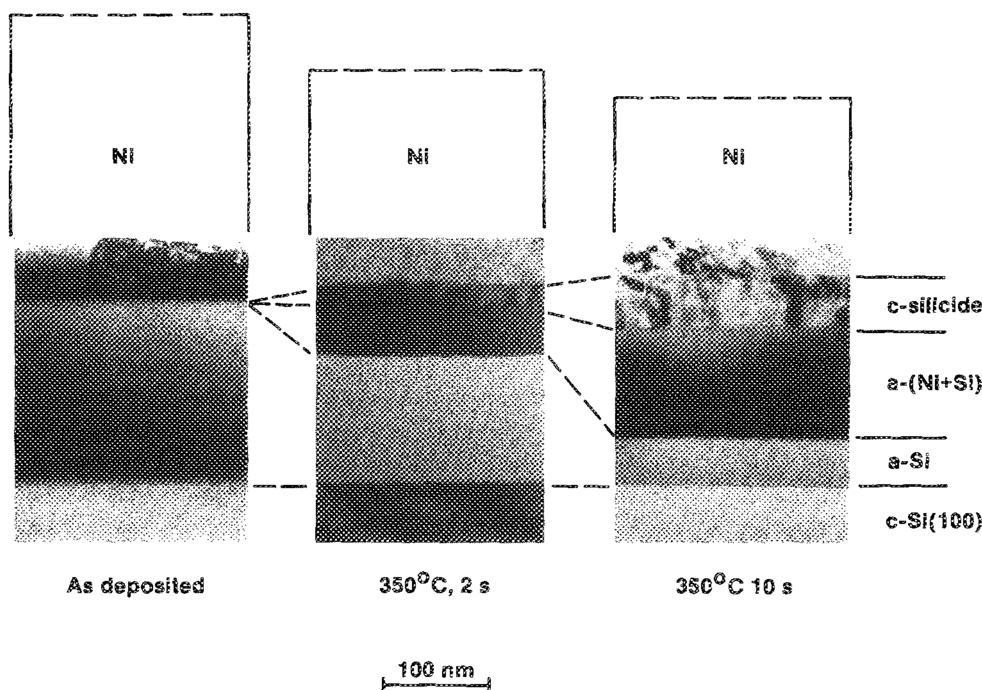

FIG. 2. Cross-sectional TEM micrographs showing the progressive side by side growth of amorphous and crystalline layers with sharp interfaces. The samples are the same as those in Fig. 1. See the corresponding RBS spectrum in Fig. 1 for compositional information.

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Ni/a-Si samples, it is quite conceivable that a sizable amount of carbon in Si may serve to impede the interfacial kinetics and growth of crystalline compounds, such as Ni_2Si. Carbon may in fact hinder the collective atomic motion, particularly of Si, required to form crystalline compounds, thereby stabilizing the amorphous phase. The generalization of this idea is that an impurity such as carbon can stabilize the stationary matrix without interfering significantly with the diffusion of the dominant moving species, thus favoring the growth of a metastable phase. It is also possible that carbon alters the free-energy relationships among the phases, in favor of the amorphous structure. Nucleation kinetics of the crystalline phase and the effect of carbon thereon must be considered in detail to determine at what stage of evolution the crystalline phase forms. At present, this question remains unresolved. A more detailed investigation of the initial stage of the reaction will prove illuminating for a better understanding of the reaction process.

Our observations in Ni/a-Si bilayers constitute an interesting contrast to those in Ni/Zr, which is a prototype system of solid-state amorphization by interdiffusion reaction in metal/metal diffusion couples. In the case of Ni/Zr, nucleation of a crystalline compound is much more difficult (requires a higher annealing temperature) than in Ni/Si. This allows the amorphous Ni-Zr phase to grow during low-temperature annealing to a substantial thickness prior to crystalline compound formation.[21] In addition, the amorphous Ni-Zr phase is richer in the dominant moving species Ni than the first nucleating equiatomic compound. This compositional sequence results in a spatial configuration of Ni/a-$(Ni + Zr)/c$-NiZr/Zr during the reaction. Once the crystalline compound nucleates, the further growth of the amorphous phase at the expense of the compound is thermodynamically unfavorable.[6] It is observed experimentally that the amorphous phase stops growing or shrinks away,[21–23] whereas the crystalline compound continues to grow. Such a thermodynamic constraint is apparently absent in our Ni/Si case, thus allowing side by side growth of both phases. Another interesting feature emerging here is the very sharp interface between the amorphous silicide and the amorphous silicon. This implies that two distinct amorphous structures with differing compositions and a positive interface tension are in metastable equilibrium at this interface.

In conclusion, we find that the presence of an impurity (e.g., carbon) in a stationary matrix (e.g., amorphous Si) can stabilize the amorphous phase induced by a solid-state interdiffusion reaction. The impurity hinders the formation of a new compound phase (e.g., Ni_2Si), but without significantly affecting the fast indiffusion of the moving species (Ni).

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