Direct observations of the nucleation and growth of $NiSi_2$ on Si (001)

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ABSTRACT: The formation of epitaxial nickel disilicide from agglomerated films of nickel monosilicide has been studied using a modified ultrahigh vacuum transmission electron microscope. Nickel films 12nm in thickness were deposited by in-situ electron beam evaporation and annealed at temperatures of up to 850ºC. We observe the nucleation of epitaxial nickel disilicide at the boundary between the nickel monosilicide and the silicon substrate at the free surface of the film. The mono: disilicide interface is then observed to propagate through the monosilicide island. We discuss our observations in terms of the relief of lattice strain in response to the volume contraction associated with this reaction.

1. INTRODUCTION

The silicon microelectronics industry relies heavily on the properties of silicon: metal silicide interfaces for front-end-process CMOS device technology (see for example Murarka (1983)). As device dimensions continue to decrease, the demands of the device architectures are rapidly approaching the performance limits of the materials presently employed. Silicidation processing typically involves the physical vapour deposition of a blanket metal layer over the Si wafer followed by annealing to form the desired silicide phase. Cobalt disilicide is currently the material of choice for the source, drain and gate contacts of CMOS FET devices, having replaced titanium disilicide for reasons of a size-dependent phase transformation between the high and low resisitivity phases (the C49 and C54 phases, respectively). The silicon consumption associated with $CoSi_2$ is high, however, and concerns about excessive junction leakage currents are an incentive to develop alternative silicidation technologies.

Nickel disilicide is a promising candidate, offering a lower temperature of formation (typically 300-400ºC) and lower silicon consumption. The principal disadvantage, however, is the relatively low thermal stability of NiSi, which is found to transform to the higher resistivity $NiSi_2$ phase above ~650ºC. In relatively thin films, the NiSi typically agglomerates prior to disilicide formation. A number of methods of suppressing the agglomeration of NiSi have been studied, including the addition of small amounts of platinum, see for example Mangelinck et al. (1999) and BF_2^+ implants (Wong et al. (2002)). In the absence of surface oxide layers prior to Ni deposition, the formation of NiSi around 300ºC is normally observed, with the subsequent formation of $NiSi_2$ between ~650-750ºC.

In this paper we report direct observations of the nucleation of $NiSi_2$ and discuss our observations in terms of strain relief at the free surface of the film.

2. EXPERIMENT

Substrates for in-situ deposition and annealing were prepared from device grade Si wafers (n-type, resistivity ~10Ωcm^{-2}) cut to dimensions of 6mm x 2mm, 200μm in thickness. The samples were

thinned to electron transparency by uniaxial dimpling followed by chemical etching in $HF:HNO_3:H_2O$ 1:3:1. Immediately prior to loading in the microscope the samples were dipped in an aqueous solution of HF (10%) to remove any surface oxide.

The sample was then transferred into the column of the electron microscope, which was a JEOL 2000V UHV TEM (base pressure ~1.5 x 10^{-10}Torr) modified for in-situ gas injection and solid source deposition (see for example Chong et al. (2003)). Deposition of a thin layer of Ni, 12nm in thickness was performed by in-situ electron beam evaporation of high purity Ni (99.9995). Upon completion of the deposition process the sample was heated (by direct current heating) at a rate of ~10°C min^{-1} to 300°C, and held for one hour. Further heating to 750°C was then performed in stages.

3. RESULTS AND DISCUSSION

In our experiments, upon heating to 300°C, the formation of NiSi was observed. Selected area diffraction patterns confirmed that the film was comprised entirely of NiSi within one hour of attaining this temperature. The film was continuous, with no voids present; it was noted that the film was composed of grains under considerable strain, as judged from diffraction contrast images recorded at this stage. Upon heating to ~550°C, the formation of voids in the NiSi film was observed along the grain boundaries, the observed contrast being consistent with grain boundary grooving which was followed by agglomeration consistent with capillary instability as discussed by Jiran and Thompson (1990) for Au thin films on fused silica. The film was now comprised of isolated islands of NiSi, as may be seen from the bright field images recorded at this stage and presented in Fig. 1. These images were taken from a video recording of the later stages of the agglomeration process, with an interval of approximately 1s between the frames presented. During this interval, the islands continue to break up, as may be seen by comparison of area 'A' in both images.

The formation of NiSi at this temperature is consistent with a number of previous reports where annealing of Ni/Si(100) was studied using techniques such as in-situ x-ray diffraction, in-situ ellipsometry as well as ex-situ TEM (see e.g. Olowolafe et al (1976), d'Heurle et al (1984), Julies et al (1999), Tinani et al (2001)).

Further heating of our sample was then performed, and attention was focused on the island marked 'I' in Fig. 1(b). At a temperature of ~650°C, the nucleation of $NiSi_2$ was observed to occur at the edge of the island, in the location marked 'N'. The newly formed NiSi: $NiSi_2$ interface propagated laterally across the entire width of the film, thereby forming two distinct NiSi: $NiSi_2$ grain boundaries. The two boundaries then propagated through the NiSi island in opposite directions until the configuration shown in the bright field image of Fig. 2(a) was attained. The transformed $NiSi_2$ portion of the island is terminated at both ends by remaining NiSi. Further annealing at higher temperatures resulted in the two NiSi: $NiSi_2$ grain boundaries finally completing their propagation through the remaining NiSi. An island comprising a single crystal of $NiSi_2$ with no grain boundaries was thus formed, as confirmed by the dark field image presented in figure 2(b), which was recorded using an $NiSi_2$ (200) reflection. The $NiSi_2$ was found to exhibit the epitaxial orientation relationship (001) $NiSi_2$ // (001)Si, [100] $NiSi_2$ // [100] Si.

We understand our observations from a consideration of the free energy of formation of $NiSi_2$. The formation of $NiSi_2$ is known to be nucleation controlled since the free energy of formation for the reaction NiSi + Si $\rightarrow$ $NiSi_2$ is small; the reaction is therefore dominated by the increase in interfacial energy $\Delta\sigma$ associated with the nucleation of $NiSi_2$ (see for example d'Heurle (1988), and d'Heurle (1989)) The reaction results in a total volume decrease of 12%, thus inducing not inconsiderable strain in the crystal lattice. The strain energy may be minimized by nucleation of the $NiSi_2$ close to the free surface of the film, where deformation of the surface can occur in order to relieve a portion of the strain energy, and thus we observe nucleation to occur at the edge of our NiSi islands. Our observations are consistent with the cross-sectional TEM observations of Wong et al. (2002) where the formation of $NiSi_2$ at the edges of NiSi islands was observed. In the present work we have observed directly the location of

the $NiSi_2$ nuclei and the subsequent propagation of the NiSi: $NiSi_2$ interface through the NiSi island (see Nath et al (2003) for further details). Propagation of this boundary can proceed rapidly by diffusion of atomic species at the temperatures involved; marker experiments have shown that diffusion of Ni is typically the dominant mass transport mechanism in both Ni_2Si, NiSi and $NiSi_2$, diffusing approximately an order of magnitude faster than Si (Tu et al. (1975), Finstad (1981) and d'Heurle (1982)).

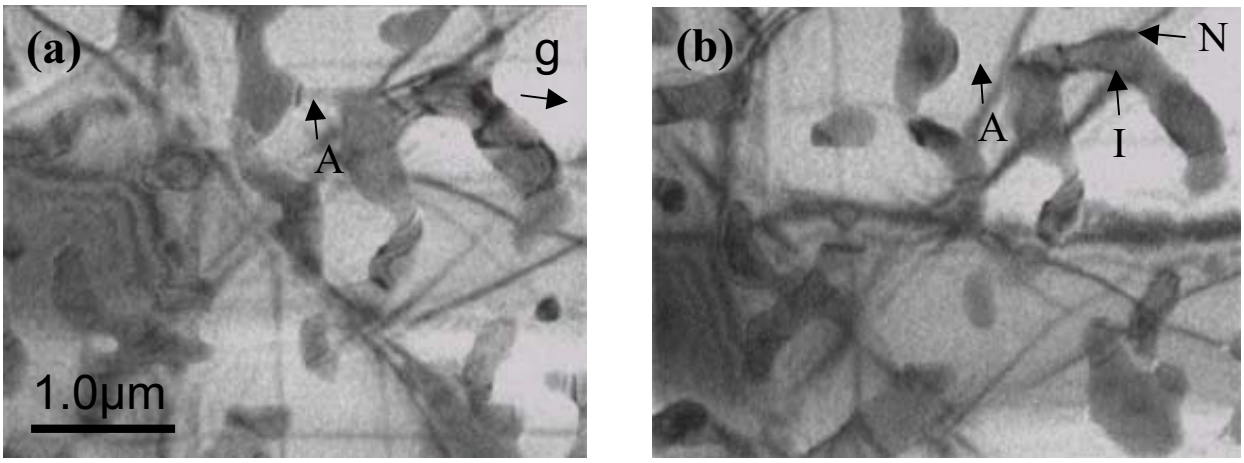

Fig. 1 Snapshots of a video showing the later stages of the agglomeration process of the initially continuous NiSi film. The time interval between the images is 1s. Comparison of area 'A' in (a) and (b) shows the continued breaking up of the film. In (b), the location of the initial nucleus of $NiSi_2$ in island 'I' is labeled 'N'.

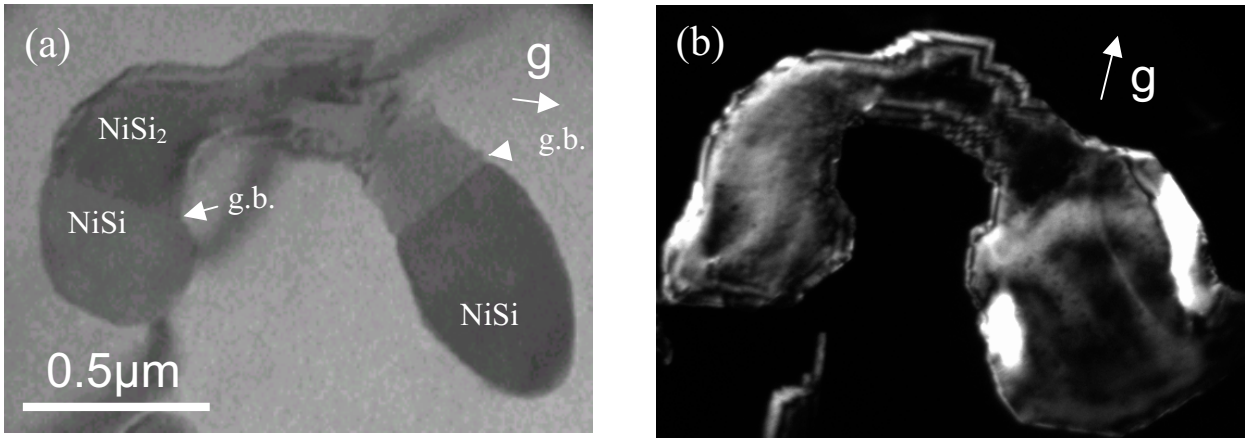

Fig. 2 (a) Bright field 220 image of the island labeled 'I' in figure 1(b) after heating to 650°C. The grain boundaries (g.b.'s) between NiSi and NiSi are labelled. (b) Dark field 200 image of the island after full transformation to $NiSi_2$.

4. CONCLUSIONS

We have successfully synthesised pinhole-free thin NiSi films on Si(001) substrates by annealing blanket Ni films 12nm in thickness in the polepiece of a UHV TEM at 300°C. Agglomeration of the NiSi films was observed at ~550°C, with the subsequent transformation to $NiSi_2$ between 650 and 700°C. Nucleation of $NiSi_2$ occurred at the edges of the NiSi islands, at the free surface of the substrate. The transformation front was observed to propagating laterally through the entire NiSi island. Our observations are understood from a consideration of the reduction in the free energy barrier for nucleation of $NiSi_2$ at the free surface of the film where enhanced strain relaxation can occur, in contrast to a location along the buried NiSi: Si interface.

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