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Overgrowth and Characterization of Epitaxial Silicon on Patterned $NiSi_2$ Grown by Molecular Beam Epitaxy

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Molecular beam epitaxy has been shown to provide high quality, $Si/NiSi_2/Si$ double hetero-structure crystals. From this growth technique, the method of burying a finger shaped $NiSi_2$ layer into the Si single crystal has been realized. The crystal orientation and quality of these double hetero-structure films have been found to be favorable for the fabrication of a new class of novel devices.

1. INTRODUCTION

Since metalic silicide films have higher electric conductivity than poly-silicon and have higher temperature stability than aluminum, they have been recognized to be promising as high performance electrodes in semiconductor devices. They are, however, primarily formed by deposition on a Si substrate under relatively poor vacuum and are in a polycrystalline phase.

Recently, such silicides as $CoSi_2$, $NiSi_2$, PtSi and Pd_2Si have been found to grow epitaxially. Epitaxially grown single crystalline silicides surpass polycrystalline silicides in conductivity, thermal stability, and reproducibility of interface properties. Moreover, for $CoSi_2$ and $NiSi_2$, a double heterostructure of Si/silicide/Si can be grown[1),] because the crystal structure and the lattice constant of these silicides are very similar to those of Si. This double heterostructure provides a new field of synthetic single crystalline multi-structure or superlattices of semiconductor and metal layers. Such structures can also be applied to form buried metal electrodes in a single crystal semiconductor layer, which would be essential for development of high performance solid state triodes such as permeable base transistors(PBTs), static induction transistors (SITs), and so on. Comparing $CoSi_2$ with $NiSi_2$, $NiSi_2$ is more attractive since it has a much smaller lattice misfit(0.4 %) to Si than $CoSi_2$(1.2%) has, thus probably generating less crystal defects in the epitaxial layer.

Previously, we reported that a highly crystalline epitaxial $NiSi_2$ film with a smooth surface morphology can be obtained on a Si substrate by using molecular beam epitaxy (MBE) technique[2)]. This paper describes the epitaxial growth and characterization of $Si/NiSi_2/Si$ double hetero-structure. It also discusses the possibility of burying the $NiSi_2$ single crystalline finger shaped electrodes in the Si single crystal.

2. EXPERIMENTS

Molecular beam epitaxy of Si and $NiSi_2$ was carried out on two inch diameter Si(111) wafers in an MBE chamber with a base pressure of $2x10^{-11}$ Torr. The substrates were cleaned by a low temperature thermal etching method at 800 °C prior to growth[3)]. This cleaning method avoids the serious problems encountered when a conventional high temperature treatment is employed. Si wafer surfaces prepared in this manner always displayed sharp 7x7 RHEED(Reflective High Energy Electron Diffraction) pattern, characteristic of a clean Si(111) surface, and no impurities could be detected by AES(Auger Electron Spectroscopy). Next, a $NiSi_2$ epitaxial layer was grown on the Si

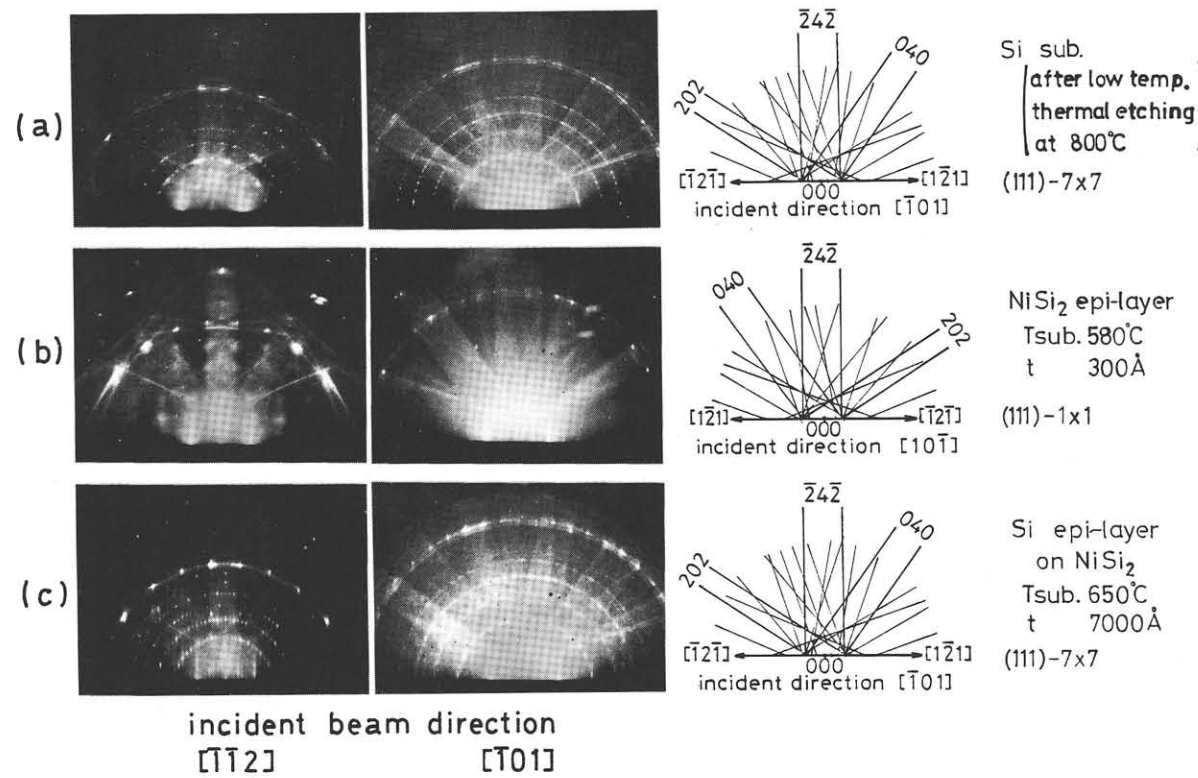


Fig.1 In situ RHEED observation of Si/NiSi$_2$/Si heteroepitaxial growth.
(a) Si substrate after thermal cleaning
(b) NiSi$_2$ epitaxial layer on Si substrate
(c) Si overgrown layer on silicide

substrate by the co-deposition of Ni and Si beams generated from two separate electron beam evaporators. A substrate temperature of 550 ~ 600 ℃ was maintained during NiSi$_2$ growth and the stoichiometric ratio of the Si/Ni beam intensity was maintained to produce these films. To bury the electrodes of NiSi$_2$ into the Si, the NiSi$_2$ layer was etched to produce 1~5 μm width fingers, similar to a PBTs base electrode configuration, using photolithography and ion milling. The wafer was cleaned once again prior to epitaxial Si overgrowth by exposure to a Si molecular beam with a rate of 0.2 Å/sec for 100 seconds, at a substrate temperature of 800 ℃. The top Si layer was grown at a substrate temperature of 650 ~ 750 ℃ and a growth rate of 1 Å/sec.

3 RESULTS and DISCUSSIONS

3.1 Si/NiSi$_2$/Si double hetero-structure

Si/NiSi$_2$/Si double hetero-structure was characterized by using in-situ RHEED and AES analyses. Figure 1 shows photographs of RHEED patterns of the substrate, NiSi$_2$ and overgrown Si layers, where incident electron beam directions are parallel to the [$\bar{1}$01] and [$\bar{1}\bar{1}$2] direction of the substrate. This observation gives important information concerning the crystal quality and crystallographic orientation of the grown layers.

Firstly, the RHEED patterns show sharp spots and clear Kikuchi bands with (111)-1x1 for NiSi$_2$ and (111)-7x7 superstructure for overgrown Si. This indicates that NiSi$_2$ and overgrown Si layers have good crystallinity. These epitaxial layers of $NiSi_2$ and Si were found to homogeneously grow all over the Si substrate and have mirror surfaces, by differential interference microscopic observations.

The crystal orientation of the $NiSi_2$ and the overgrown Si layer can be determined by Kikuchi band pattern analysis. Schematic patterns of the Kikuchi bands corresponding to the photographs of the Si substrate, $NiSi_2$ layer and overlayer Si are presented in the figure when the incident beam is along [$\bar{1}$01] direction of the substrate. For the $NiSi_2$ film, the Kikuchi pattern coincides with that expected when the incident beam is along [10$\bar{1}$] direction. So it is concluded that the $NiSi_2$ film is type B, that is, rotated 180 degrees about the surface normal [111] axis with respect to the substrate, and that the overgrown Si also rotates 180 degrees with respect to the $NiSi_2$, and has the same orientation as the substrate. This fact is vrey favorable for the perfectness of the interface between the overgrown Si and the substrate, which are formed when finger shaped $NiSi_2$ grids are buried. That is, the interface such as twin boundary is not formed in the electrical active region. This is very promising for device applications.

3.2 Burying the finger shaped $NiSi_2$ electrodes in Si

In order to make buried $NiSi_2$ grids in the Si, the MBE-grown $NiSi_2$ film was etched in the finger shape with 1 ~ 5 μm width by using photolithography and Ar^+ ion milling. Since the surface of $NiSi_2$(patterned)/Si(sub) was contaminated due to the treatment of patterning, the cleaning of the surface prior to the MBE growth was very important to obtain high quality of overgrown epitaxial Si. Figure 2 shows the Auger spectra for the cleaning processes of the $NiSi_2$(patterned)/Si(sub). After chemical etching by dilute HF sulution, main contaminants on both the $NiSi_2$ and Si regions are oxygen and oxide layers with thickness of about 20 Å and 3 Å are formed, respectively(Fig.2-(a)). The oxide still remains on the $NiSi_2$ region even after thermal etching at 800 ℃, although the oxide on Si is easily removed(Fig.2-(b)). This oxide remained on

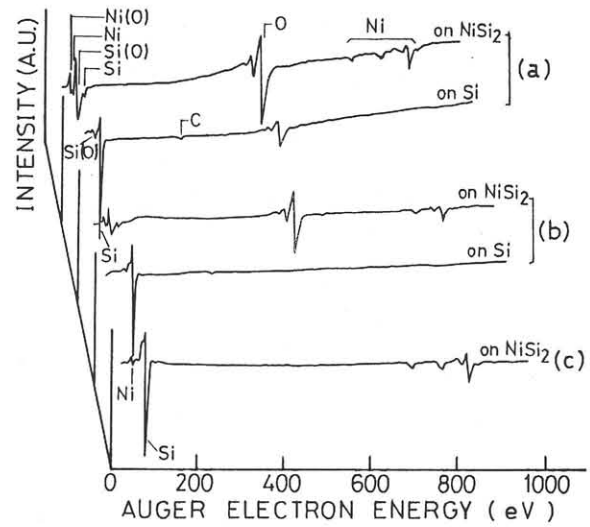
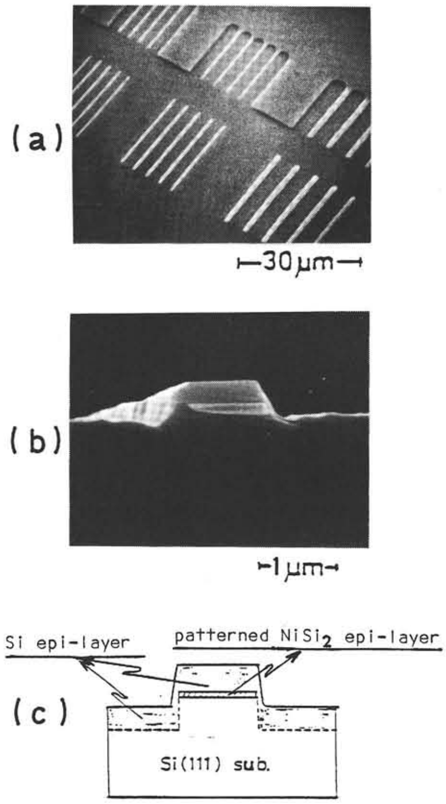


Fig.2 Auger analysis of surface cleaning process for $NiSi_2$(patterned)/Si(sub)
(a) after chemical etching by dilute HF solution
(b) after thermal etching at 800 ℃
(c) after Si beam exposure at 800 ℃

the $NiSi_2$ could be removed by chemical reaction with the Si molecular beam. Figure 2-(c) is the AES spectrum after exposure of Si beam at 0.2 Å/sec rate for 100 seconds at 800 ℃. Auger peaks observed are those of Ni and Si atoms only from $NiSi_2$. This surface gives the clear (111)-1x1 RHEED pattern quite similar to that in Fig.1-(b).

After this treatment, Si overlayer was grown on this patterned substrate. Figure 3-(a) is an SEM image showing the surface structure of Si(overgrown)/$NiSi_2$(patterned)/Si(sub). Figure 3-(b) is an SEM image of a cross-section of the sample, and the schematic structure of this image is shown in Fig.3-(c). The clear (111)-7x7 superstructure was observed by the in situ RHEED measurement and it can be said that the overgrown Si layer on the $NiSi_2$(patterned) film is single crystal. This means that $NiSi_2$ single crystalline electrodes can be buried in the Si single crystal.

Since the crystal quality of the overgrown Si crystal dominates final device characteristics, incorporation of Ni atoms in Si layer was studied



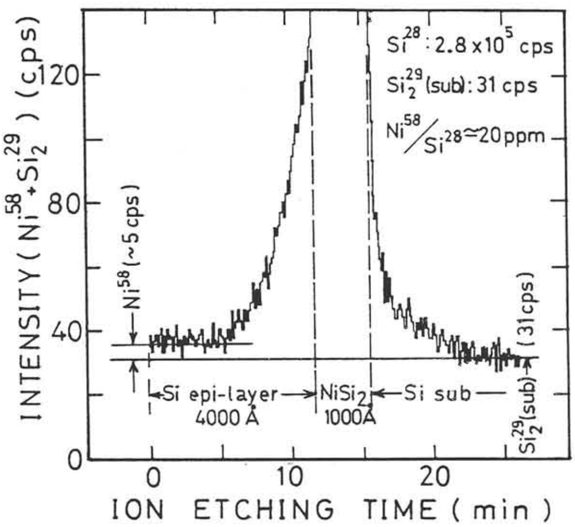


Fig.4 Depth profile of Ni impurity in $Si/NiSi_2/Si$ heterostructure by SIMS analysis

Fig.3 SEM microphotographs of buried finger shape $NiSi_2$ electrodes in Si crystal
(a) surface structure
(b) cross-section view
(c) schematic structure of cross-section with buried $NiSi_2$ grid layer in Si

by AES and SIMS methods. In situ AES analysis showed that Ni was not detected on the surface of the overgrown Si layer. Since the sensitivity of AES is up to 0.1 % of constituent atoms, SIMS measurement was also carried out to detect impurities at much higher sensitivity. Figure 4 shows the depth profile of Ni for Si(overgrown)/$NiSi_2$(patterned)/Si(sub) double hetero-structure. A small number of Ni atoms less than 20 ppm were detected in the overgrown Si. These Ni atoms may be due to the out-diffusion from the $NiSi_2$ layer during growth at 750 °C. The Ni out-diffusion is undesirable for device applications, and then the growth temperature should be reduced as low as possible. The optimization of the growth conditions is now in progress.

4. SUMMARY

It has been shown that MBE can provide considerably high quality crystal of $Si/NiSi_2/Si$ double hetero-structure. Buring the finger shaped $NiSi_2$ film in the Si single crystal has been carried out by using above double hetero-epitaxial growth technique. Crystal orientations and qualities of the growth films of double hetero-structure are favorable for fabrication of a new class of novel devices employing buried metal electrodes in semiconductor.

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