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Ultra-Smooth Heteroepitaxial $NiSi_2$ Films on Silicon Grown by Molecular Beam Epitaxy

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Highly crystalline epitaxial $NiSi_2$ films with smooth surface morphology have been obtained on silicon by using molecular beam epitaxy (MBE) technique. Stoichiometric deposition of Ni and Si beams allows $NiSi_2$ heteroepitaxial growth on atomically clean surfaces at temperatures as low as 550°C. The film may be applicable to novel devices employing buried metal electrodes in semiconductors.

1. Introduction

Metal silicide films have been commonly used in the semiconductor industry as ohmic or Schottky barrier contacts. They are primarily formed by deposition on Si substrates under relatively poor vacuum and are in polycrystalline phase. Recently, such silicides as $CoSi_2$, $NiSi_2$, PtSi and Pd_2Si have been found to grow epitaxially. Epitaxial silicides surpass conventional silicides in conductivity, thermal stability and reproducibility of interface properties. In particular, cobalt disilicide has become the focus of attention due to the fact that the double heterostructure of $Si/CoSi_2/Si$ can be grown with it$^{1)}$. Nickel disilicide is also attractive since it has much smaller lattice misfit (~0.4%) to Si than $CoSi_2$ (~1.2%). However, only granular epitaxial films have been obtained so far$^{2)}$ except small scale fundamental deposition experiments$^{3)}$.

We have employed molecular beam epitaxy (MBE) to obtain high quality $NiSi_2$ films on standard Si wafers. The heteroepitaxial silicide films that have been grown suggest the possibility of a new field of synthetic single crystalline multistructures or superlattices of semiconductor and metallic layers, as well as a new class of novel devices. The films are especially promising as buried metal electrodes in semiconductors which are essential to the development of high performance solid state triodes such as permeable base transistors (PBTs), static induction transistors (SITs), and so on.

2. Experimentals and discussions

All depositions were carried out in a UHV chamber (VG 366 MBE system) with a base pressure of $2x10^{-11}$Torr Silicon and nickel beams were separately generated by e-guns. Surface treatment of substrates prior to MBE growth is very important to facilitate layer growth and to obtain smooth-surface epitaxial films. Low temperature treatment is also required in order to avoid thermal diffusion of impurities and generation of lattice defects such as dislocations and slip lines. Thus, we employed a low temperature (<800°C) thermal cleaning method$^{4)}$ whereby clean surfaces exhibiting super structures in reflection high energy electron diffraction (RHEED) measurements were obtained and where no discernible traces of contaminants were observed in Auger electron spectroscopy (AES) measurements.

Silicides were formed on silicon wafers under a variety of conditions. We will firstly describe the results of room temperature deposition of pure metal on Si (100) substrates and reaction at elevated temperatures. Figure 1 shows RHEED patterns observed in-situ and deferential interference contrast (Nomarski) microphotographs of grown films. Nickel films grown on clean

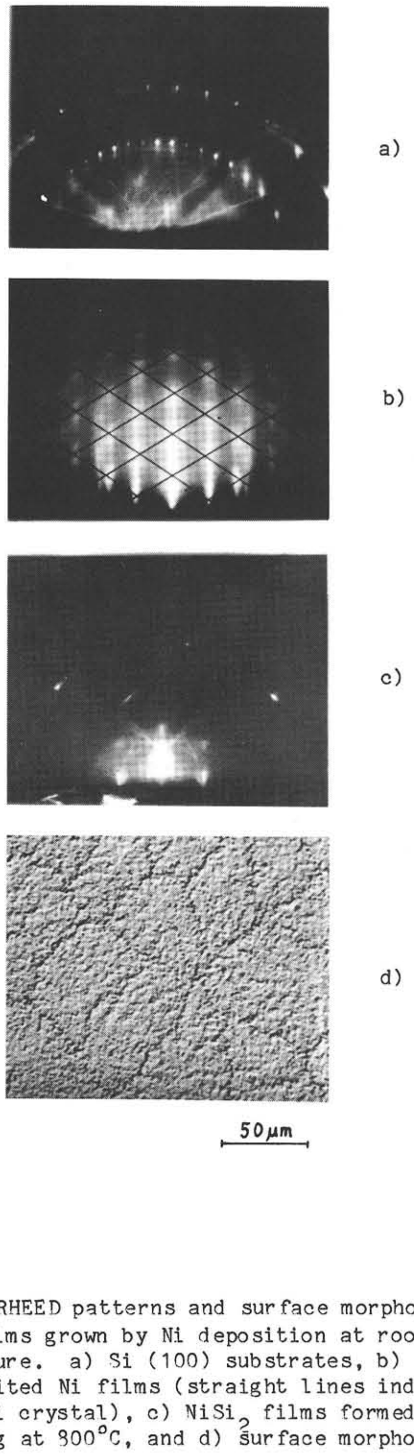


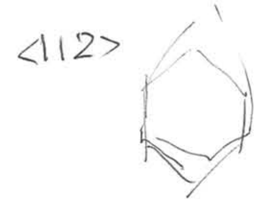
Fig. 1 RHEED patterns and surface morphology of $NiSi_2$ films grown by Ni deposition at room temperature. a) Si (100) substrates, b) as-deposited Ni films (straight lines indicate single Ni crystal), c) $NiSi_2$ films formed by annealing at 800°C, and d) surface morphology of $NiSi_2$ films

Si(100)-2x1 gives diffused diffraction spots corresponding to single Ni crystal before heat treatment. Although it is striking and certainly interesting that single crystal growth of metal films takes place at room temperature on Si substrates, this is not the subject of this paper and those details will be discussed elsewhere. After heating films at temperatures above 600°C, single $NiSi_2$ films were epitaxially formed as seen in this figure. However, as can also be seen in this figure, the heteroepitaxial film surface is granular. Obtaining smooth $NiSi_2$ film by this method proved to be very difficult.

The direct formation of $NiSi_2$ by deposition of pure metal at elevated temperatures was then examined. Figure 2 shows RHEED patterns and Nomarski microphotographs of grown films. Except for the 450°C sample, all films are single crystals. As can be seen in this figure, the RHEED pattern becomes sharper with increasing substrate temperature. Surface morphology follows a similar temperature evolution, and the smoothest, almost featureless, films are grown at 650°C. Above this temperature, however, roughness is pronounced and flat-topped nuclei are observed, while the RHEED pattern remains sharp as shown in Fig.2. The edges of flat-topped nuclei are along the ⟨110⟩ crystallographic direction.

More smooth $NiSi_2$ films than those in Figs.1 and 2 were grown by codeposition of nickel and silicon beams. Figure 3 shows the results obtained under conditions where a stoichiometric deposition ratio of 1:2 was employed at a substrate temperature of 550°C, where the growth rate was about 1 Å/sec and the thickness was 1000 Å. Extremely sharp RHEED patterns including diffraction spots and Kikuchi lines are observed. There are some indications in the RHEED pattern that the film is planarly continuous and has a flat surface. The film is completely featureless under Nomarski examination as is seen in this figure. This $NiSi_2$ film is to our knowledge the smoothest among heteroepitaxial silicides reported so far.

When the beam ratio varied from the stoichiometry, the surface morphology was not strongly affected, but gradually became poor. A



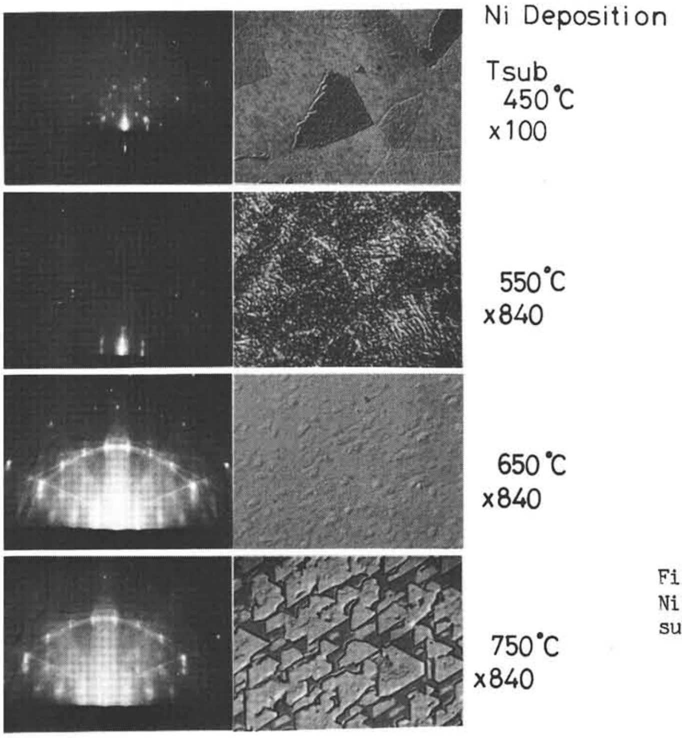


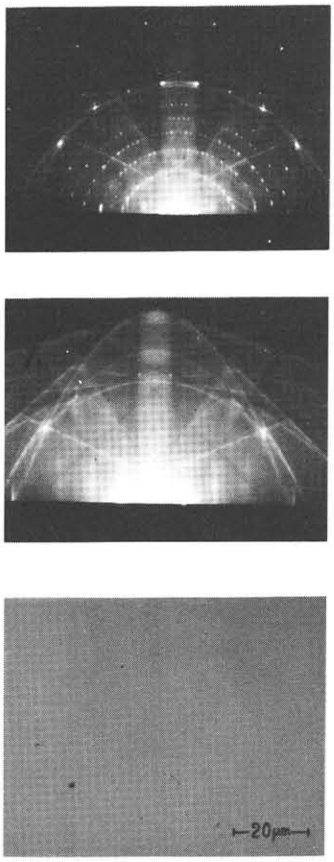
Fig. 2 RHEED patterns and surface morphology of $NiSi_2$ films grown by Ni deposition on Si (111) substrates at elevated temperatures.

silicon beam shortage could be compensated for by silicon diffusion from the substrate, but some features appear on the surface. On the other hand, when the Si beam is larger, excess silicon segregates along the ⟨110⟩ direction in the film.

The interface between the $NiSi_2$ film formed by the codeposition technique and Si substrate was examined using the sputtering AES method and was found to be sharp enough. The transition region width was well below the AES resolution limit (<70Å).

It is well known5) that even if nickel films are deposited on Si substrates under poor vacuum conditions, $NiSi_2$ films are formed after heat treatment. The annealing in this case always results in phase change of nickel silicides. Namely, the growth of Ni_2Si first occurs at temperatures between 250°C and 350°C. It is followed by the formation of NiSi at temperatures between 350°C and 775°C, and above 775°C the $NiSi_2$ film is finally formed. This $NiSi_2$ film is generaly polycrystalline and of mixed type-A and type-B orientations on a (111) substrate. However, the reaction of nickel silicides in this study does not follow the same pattern. Intermediate states (Ni_2Si and NiSi) are not generated, and the final phase of $NiSi_2$ is directly formed. Moreover, the minimum formation temperature of $NiSi_2$ (~450°C) is far below that for conventional ones (775°C). According to photoemission studies on nickel silicon interfaces6), reaction between a few monolayers of nickel and silicon substrates takes place and silicides are formed even at room temperature, if the substrate surface is kept atomically clean. At elevated temperatures, this reaction is enhanced and the stable $NiSi_2$ phase appears without formation of intermediate phases. Epitaxial temperature could be reduced on a clean surface since the surface cleanliness allows nickel atoms to easily migrate to regions where crystal growth takes place.

Silicon films were overgrown on $NiSi_2$ silicides by cutting off the metal beam and maintaining the silicon deposition. The overgrown



Si Substrate
(after low-temperature thermal etching at 800°C)
(111) 7x7

Ni-Si Codeposited Film
Tsub 550°C
Ni/Si ~1/2

Differential Interference of Photomicrograph of Heteroepitaxial $NiSi_2$ Film

Fig. 3 RHEED patterns and surface morphology of $NiSi_2$ films grown by codeposition (MBE) on Si (111) substrates.

film gave super structure patterns, 7x7, in RHEED measurements. This suggests that single crystalline Si(epi)/$NiSi_2$(epi)/Si(sub) multistructures are fabricated. The quality of overgrown Si films is now under investigation.

3. Summary

We have shown that MBE can be used to grow highly crystalline silicide layers on silicon. Stoichiometric deposition of Ni and Si beams gives especially high quality heteroepitaxial layers at temperatures as low as 550°C. Studies of these structures will lead to an understanding of interfaces and epitaxy of silicides as well as offering opportunities for application. A study of the feasibity of $NiSi_2$ film for use as a buried layer in a manner similar to that for PBTs is now in progress.

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