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MBE-Grown $NiSi_2$/Si Heterostructure and its Schottky Properties

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The correlation between Schottky contact properties of MBE grown $NiSi_2$ and its growth conditions is studied. A strong dependence of the Schottky contact ideality factor, n, upon the surface morphology and growth conditions of $NiSi_2$ film is found. It is verified that uniform $NiSi_2$ film can be grown at temperature lower than 600 °C and that it is very important to maintain stoichiometrical growth conditions. The smooth $NiSi_2$ films grown in this manner are confirmed to give good Schottky characteristics.

1. INTRODUCTION

There is currently a great deal of interest in metal silicides largely because of their facility for application in semiconductor devices. Among them, $CoSi_2$ and $NiSi_2$ are especially attractive since they can be epitaxially grown on silicon crystals, enabling Si/silicide/Si multi-structures to be formed. This type of double heterostructure can be utilized in the fabrication of high performance solid state devices with buried metal electrodes such as permeable base transistors (PBTs), static induction transistors (SITs), and metal base transistors (MBTs).

$NiSi_2$ has much smaller lattice misfit (0.4%) to Si than $CoSi_2$ (1.2%). Consequently, it is expected that few defects will be generated at the silicide/Si interfaces and also in epitaxial layers. Recently, the authors have reported[1)] that a single crystal $NiSi_2$ film with a very smooth surface and good crystallinity can be fabricated on a Si substrate by means of molecular beam epitaxy (MBE). It has been also reported[2)] that monocrystalline finger-shape $NiSi_2$ grids can be embedded in Si crystals, and the high potential for development of new devices through the use of this method has been demonstrated. Here we report on studies regarding the electrical properties of interfaces between epitaxial $NiSi_2$ films and silicon to determine the correlation between Schottky contact properties and growth conditions. Our method of growing $NiSi_2$ films is co-deposition of Ni and Si molecular beams (i.e., the MBE method), in which the growth conditions such as silicide layer composition, substrate temperature, and growth rate are precisely controlled.

2. EXPERIMENTS

Various kinds of $NiSi_2$ films were grown on Si(111) wafers of 2 inch diameter in an MBE chamber with a base pressure of 2×10^{-11} Torr. The Si substrates were cleaned by the low-temperature thermal etching method[3)] at 830 °C prior to growth. Si surfaces prepared in this manner displayed sharp (7x7) RHEED (reflection high energy electron diffraction) patterns characteristic of Si(111) clean surfaces, and no impurities were observed by Auger electron spectroscopy (AES) measurements. The substrate temperature was maintained constant between 540 °C and 700 °C during $NiSi_2$ growth. Ni and Si beams were generated from two separate electron beam evaporators, and the beam intensity ratio was carefully controlled so as to remain constant during growth. Total thickness of evaporated Ni and Si was about 1000 Å. After the growth, RHEED and AES measurements were carried out in situ to examine the crystallinity and composition of the films in the MBE chamber. A differential interference microscope and a scanning electron microscope (SEM) were used to observe surface morphology of the grown films. Cross sectional microstructures of silicides were

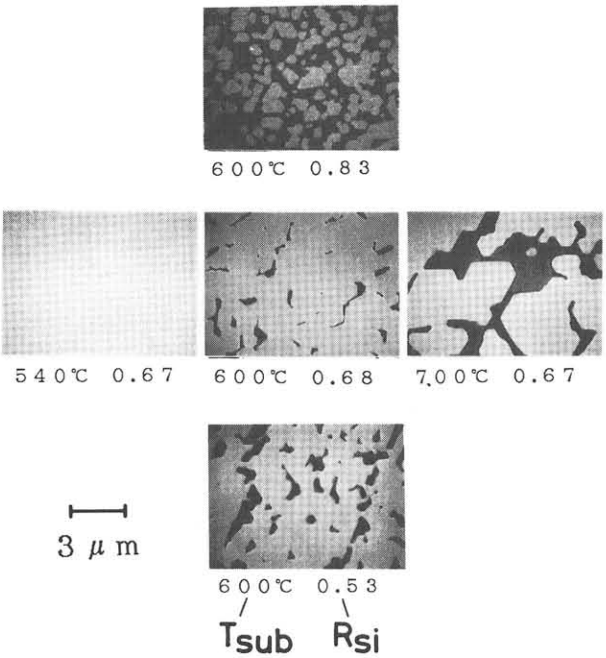

Fig. 1 Surface morphology of $NISi_2$ films grown under various conditions observed by SEM. T_{sub} is substrate temperature during growth, R_{si} is Si molecular beam intensity ratio.

investigated by a transmission electron microscope (TEM). Schottky properties were evaluated by current-voltage measurement of $NiSi_2$/Si diodes fabricated by mesa-etching of $NiSi_2$ films to form 60 to 100 μm square patterns.

3. RESULTS and DISCUSSION

Figure 1 shows SEM photographs of silicide films grown under various conditions. Silicon molecular beam intensity ratio, R_{si}, is defined as (Si beam intensity) / (Ni beam intensity + Si beam intensity). The value of R_{si}=2/3 corresponds to $NiSi_2$ stoichiometrical growth condition. It is seen in this figure that when the molecular beam intensity ratio is changed, stoichiometrical growth produces a film with a structureless surface. This surface is smoother than any other surface produced here to fore. The surface morphology, moreover, becomes better with decreasing substrate temperature.

Almost all films show $NiSi_2$(1x1) structure in RHEED patterns as shown in Fig.2(a). The exception is the film grown under Si-rich condition (R_{si}=0.83, T_{sub}=600°C in Fig.1) which exhibits the RHEED pattern consisting of a $NiSi_2$(1x1) and Si(7x7) superstructure as shown in Fig.2(b).

The film grown at 540°C under stoichiometrical conditions gave an Auger spectrum (a in Fig.3) characteristic of single crystalline $NiSi_2$. However, the other films showed Auger spectra slightly different from bulk $NiSi_2$, one example of which is shown in Fig.3. The intensity ratio of Ni(MVV) Auger transition to the Si(LVV) transition was found to depend upon growth conditions. Figure 4 shows the relative intensity of Ni(MVV) peak to Si(LVV) peak as a function of substrate temperature and molecular beam intensity ratio. It can be seen in this figure that Ni content in the film decreases with increasing substrate temperature and with increasing Si molecular beam intensity ratio.

From these results, the films are characterized as follows. The film grown at 540°C under stoichiometrical conditions is a uniform single crystal $NiSi_2$ with a flat surface. The interface between this epitaxial film and the silicon substrate has an atomically flat structure as shown in Fig.5(a). In other words, the layer growth takes place under this growth condition. At substrate temperatures higher than 600℃, the film is also single crystal $NiSi_2$, but the morphology becomes worse. From AES results, it is evident that the Ni content of the film is smaller than that of the uniform $NiSi_2$ film, which means that the $NiSi_2$ layer conglomerates and a silicon substrate surface appears. The white and black areas in Fig.1 correspond to $NiSi_2$ and silicon, respectively. Cross-sectional TEM clearly shows

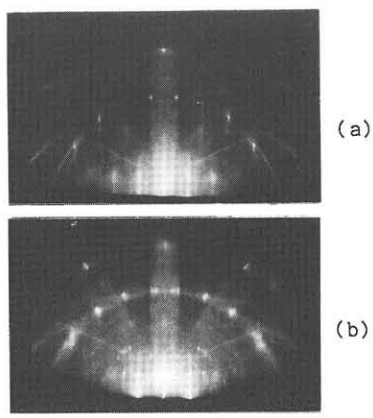

Fig. 2 RHEED patterns of $NiSi_2$ films grown at (a) T_{sub}=540°C, R_{si}=0.67, and (b) T_{sub}=600°C, R_{si}=0.83.

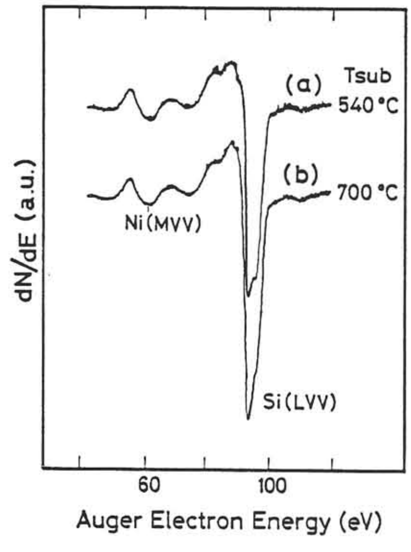

Fig. 3 Auger spectra of $NiSi_2$ grown at R_{si}=0.67 and at (a) T_{sub}=540 °C, (b) T_{sub}=700 °C.

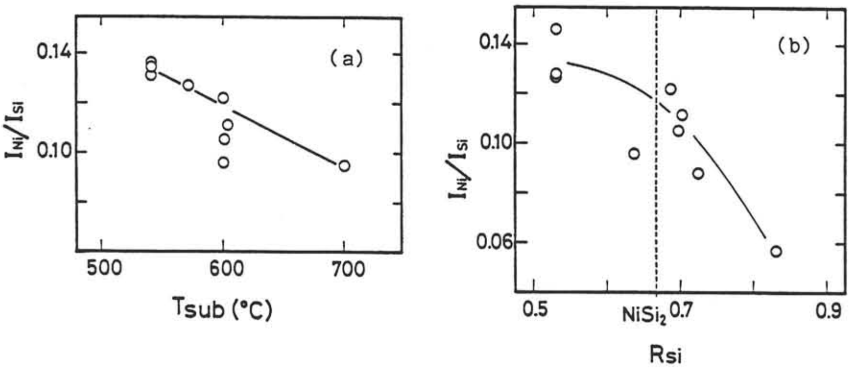

Fig. 4 Relative intensity of Ni(MVV) peak to Si(LVV) peak as a function of (a) growth temperature, T_{sub}, and (b) Si molecular beam intensity ratio, R_{si}.

the conglomeration of the $NiSi_2$ film and existence of holes in the film, as shown in Fig.5(b). In the film grown under Si-rich conditions (R_{si}=0.83, T_{sub}=600 °C in Fig.1), it can be seen from RHEED and AES measurements that the silicon content is very high. The TEM revealed that $NiSi_2$ crystallites (white areas in Fig.1) exist in the silicon matrix, as seen in Fig.5 where the dark regions correspond to $NiSi_2$ crystallites. In this growth condition, part of the evaporated Si reacts with Ni to form $NiSi_2$, but excess Si atoms epitaxially grow and form a Si single crystal.

On the other hand, the film grown under Ni-rich conditions (R_{si}=0.53, T_{sub}=600 °C in Fig.1) is a $NiSi_2$ single crystal, although the surface morphology is bad. AES shows that Si content of the film is comparable to uniform $NiSi_2$ films. As can be seen in Fig.5(d), thin $NiSi_2$ films exist even in the bottom of grooves of the film and no silicon appears on the film surface. It is well known that even if only Ni beams are irradiated on silicon substrates, $NiSi_2$ films are formed after heat treatment. In this case, Si is supplied from substrates and form $NiSi_2$. This is a kind of solid phase epitaxy (SPE) of $NiSi_2$ films. However, conglomeration of $NiSi_2$ layers tends to take place and the surface morphology becomes rough. Under the Ni-rich condition, SPE-like growth mechanism occurs and $NiSi_2$ might be formed.

Schottky barrier height and the ideality factor of the diode have been measured as a function of both substrate temperature during growth and molecular beam intensity ratio. Barrier height was found to fall in the range from 0.60 to 0.75 eV with significant deviation. Virtually no systematic dependence on substrate temperature or beam intensity ratio was seen. Recently, the correlation of Schottky barrier height and microstructure has been investigated[4] for epitaxial $NiSi_2$ on Si(111) interfaces and it has been reported that near perfect interfaces (either type-A or type-B), provide high barrier height (0.78 eV), while less perfect silicides with lattice defects or impurities yield barrier heights less than 0.7 eV. $NiSi_2$ films grown by MBE have been shown to be type-B where the crystal is rotated 180° with respect to the normal of the Si substrate[1]. The surface of epitaxial $NiSi_2$ grown under a stoichiometrical condition is very smooth and featureless, and the interface is proven to be atomically flat from TEM measurements. However, the fact that the barrier height of this film is a little lower than the ideal barrier height of 0.76 eV suggests that interfaces may contain some defects or impurities which have not been detected yet.

Figure 6 shows the Schottky diode ideality factor, n, as a function of both substrate temperature and molecular beam intensity ratio. It can be seen that the value of n approaches unity as substrate temperature becomes less than 600 °C and as the beam intensity ratio reaches the stoichiometric value of $NiSi_2$. This result suggests that the ideality factor is sensitive to the surface morphology of $NiSi_2$ films and microstructure of the interfaces. At higher substrate temperatures or under Ni-rich conditions, diffusion of Ni atoms into Si substrate easily takes place and generates impurity centers and defects. Moreover, in the films where $NiSi_2$ layer conglomeration is observed, many steps are seen at the interface, especially around the grooves in the film as shown in Fig.5(b). It is very likely that many defects which deteriorate the Schottky properties and degrade the ideality factor exist.

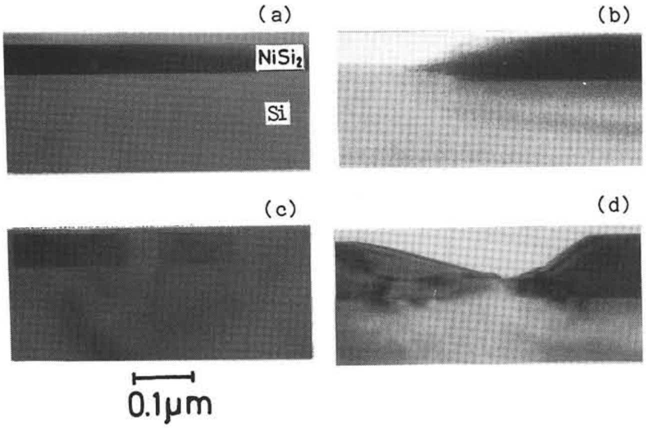

Fig. 5 Cross-sectional TEM photographs of samples grown under various conditions.

(a) T_{sub}=540°C, R_{si}=0.67, (b) T_{sub}=700 °C, R_{si}=0.67, (c) T_{sub}=600 °C, R_{si}=0.83, (d) T_{sub}=600 °C, R_{si}=0.53.

4. CONCLUSION

We have investigated the correlation between $NiSi_2$/Si Schottky properties and growth conditions. It has been shown that, (A) under Ni-rich conditions, SPE-like growth occurs and the $NiSi_2$ film becomes rough, (B) under Si-rich conditions, $NiSi_2$ crystallites are dispersed in a Si matrix, and (C) at higher growth temperatures, $NiSi_2$ is formed by MBE growth, but the layer conglomerates and a Si substrate appears. In these cases, $NiSi_2$/Si Schottky characteristics are poor. Uniform $NiSi_2$ films can be grown at temperatures lower than 600°C and stoichiometrical growth conditions must be maintained in as precise a manner as possible. It is confirmed that the smooth $NiSi_2$ films grown in this manner have good Schottky characteristics. Using TEM, moreover, it could be proved that the epitaxial $NiSi_2$/Si interface is abrupt and atomically smooth. These results show promise for applications in a new class of novel devices employing heteroepitaxial layers.

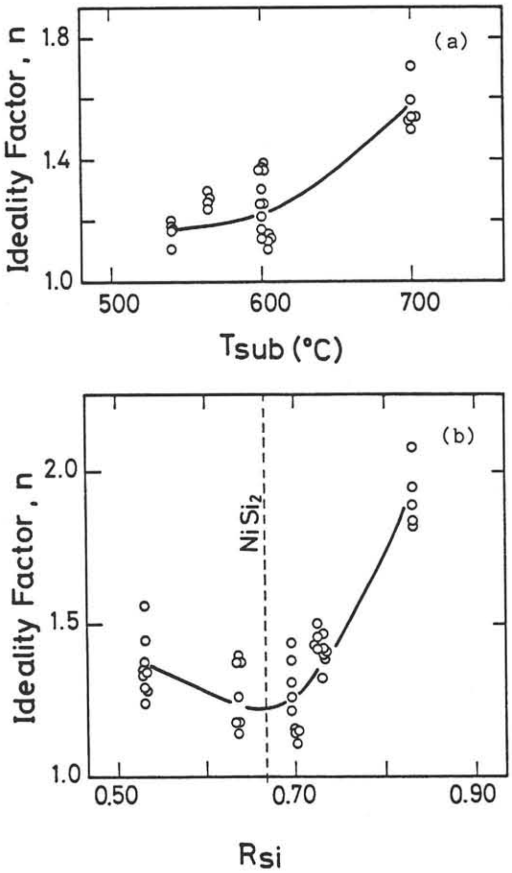

Fig. 6 Ideality factor, n, as a function of (a) growth temperature, T_{sub}, and (b) Si molecular beam intensity ratio, R_{si}.

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REFERENCES

1) A. Ishizaka, Y. Shiraki, K. Nakagawa, and E. Maruyama, 15th Conf. Solid State Devices and Materials, (Tokyo, 1983) p.15.
2) A. Ishizaka, and Y. Shiraki, Jpn. J. Appl. Phys., 23, L499 (1984).
3) A. Ishizaka, K. Nakagawa, and Y. Shiraki, MBE-CST-2(Tokyo, 1982) p.183.
4) M. Liehr, P. E. Schmid, F. K. LeGoues, and P. S. Ho, Phys. Rev. Lett., 54, 2139 (1985).