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$Si/CoSi_2/Si(100)$ heteroepitaxial growth by molecular beam epitaxy and novel solid phase epitaxy

Xin-Ping Qu, Guo-Ping Ru and Bing-Zong Li
Department of Electronic Engineering, Fudan University, Shanghai 200433, China
Jie-Qin and Zui-Min Jiang
State Key Laboratory of Applied Surface Physics, Fudan University, Shanghai 200433, China
Paul Chu
(Applied Physics Department, City University Of Hong Kong, Hong Kong, China)

Abstract: A new approach to fabricate $Si/CoSi_2/Si$ heterostructure is presented. By incorporation of novel solid phase epitaxy with molecular beam epitaxy (MBE), an epitaxial $Si/CoSi_2/Si(100)$ double heterostructure has been grown. With Co/Ti/Si ternary solid state reaction and subsequent surface treatment, high quality $CoSi_2$ surface is obtained, on which a crystalline Si layer is epitaxially grown by MBE. The double epitaxial heterostructure is confirmed by Rutherford backscattering spectroscopy and transmission electron microscopy measurements.

Introduction

Recent years epitaxial growth of Si / metal silicides / Si heterostructure has attracted much interest for the possibility of realizing a novel class of devices such as permeable base transistors[1] and new type of photodiode device[2]. Among the metal silicides, cobalt disilicide, having potential application in deep sub-micron device technology, is one of the most favorite candidates for such epitaxial growth because of its good lattice match to silicon. $CoSi_2$ crystallizes in the CaF_2 lattice structure with a lattice mismatch with respect to Si of -1.2% at room temperature. Despite this promising structural compatibility, epitaxial growth of $CoSi_2$ on Si(100) is still not a mature technique . Furthermore, the overgrowth of Si is more difficult due to the lower surface energy of Si than that of $CoSi_2$. Various techniques such as molecular beam epitaxy (MBE)[3], Ion beam synthesis(IBS)[4] and molecular beam allotaxy(MBA)[5] have been studied for the purpose.

Solid phase reaction of Co/Ti/Si ternary system is investigated by several groups.[6,7] Annealing of Co/Ti/Si structure in N_2 ambient results in an epitaxial growth of $CoSi_2$ layer on both Si(100) and Si(111) substrates. This new technique has an advantage of being compatible with the current self-aligned silicide(Salicide) technology for ultra-large scale integrated circuit (ULSI). In this paper we report the results of the incorporation of such novel solid phase epitaxy with MBE to grow $Si/CoSi_2/Si$ structure.

Experimental

N-type Si (100) wafers with a resistivity of 5-8 Ω•cm were used as the starting substrates. A standard RCA cleaning procedure was adopted, followed by a short-time etch in diluted HF in order to remove the native oxide from the wafer surface. Immediately after cleaning, the wafers were loaded into Oxford ion beam sputtering system equipped with Kaufman ion source. The base pressure of the vacuum system was 3×10^{-7} torr. The typical working Ar pressure was 5×10^{-5} torr. The energy of Ar ion beam was 1000 eV and the beam current was 50～65mA. The structure of the as-deposited samples is Co(15nm) / Si(4nm)/ Ti(3nm)/ Si(100).

The wafers with a multilayer on top were then annealed in a high purity N_2 ambient using a KST-3 rapid thermal annealing (RTA) system. Two step annealing with a selective etch in between was carried out. The wafers were first annealed at 700°C, then immersed into $H_2SO_4+H_2O_2$ solution at 120°C for 10 minutes to remove the unreacted Co, Ti, finally annealed at temperature between 850 and 1000°C. After a proper surface treatment samples were loaded into a Riber MBE system to grow the top Si layer.

The prepared $Si/CoSi_2/Si$ samples were analyzed by 2MeV He^+ Rutherford backscattering spectroscopy (RBS) and transmission electron microscopy (TEM). Channeling effect spectroscopy of RBS, cross-section TEM (XTEM) and selective area diffraction (SAD) were employed to characterize the crystalline quality.

Results and discussion

The starting point for the formation of the $Si/CoSi_2/Si$ heterostructure is the growth of a high quality $CoSi_2$ layer. In Co/Si/Ti/Si solid state epitaxy, proper layer structure and annealing procedure are the keys for achieving high quality $CoSi_2$. In previous paper, we have reported that the channeling yield minimum(χ_{min}) of $CoSi_2$ obtained by this method is about 5.2%[8]. Furthermore, the surface smoothness of $CoSi_2$ is of vital importance to the subsequent heteroepitaxial quality of Si by MBE. The surface treatment applied in present experiment can be

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divided into two steps: ex-situ etching and in-situ thermal treatment in MBE chamber. When Co/Si/Ti/Si is reacted in N_2 ambient at high temperature, Co atoms diffuse towards the substrate interface to form single-crystalline CoSi$_2$, while Ti atoms diffuse out to the top surface to form a TiN top surface layer and a thin poly-crystalline CoTiSi(O) alloy layer in between[9].

To remove the outermost TiN and CoTiSi(O) from the surface, the wafers were etched by 500eV Ar^+ ion milling followed by a standard RCA cleaning and dipping in a diluted HF solution. TEM shows that after ex-situ etching the CoSi$_2$ layer is about 10nm with flat surface. Such ex-situ treatment resulted in a clear spot pattern of Reflection High Energy Electron Diffraction (RHEED) when samples were loaded into MBE system. Prior to the growth of Si, the CoSi$_2$/Si substrate first is heated to remove possible residual oxide, under the in-situ monitoring by RHEED. The RHEED pattern doesn't change much until the substrates are heated to 800°C. When the temperature of substrate reaches higher than 800°C, the RHEED spots elongate and a typical 1×2 reconstruction pattern appears. Fig. 1 shows the RHEED pattern of a CoSi$_2$/Si substrate after 10 minute annealing at 850°C.

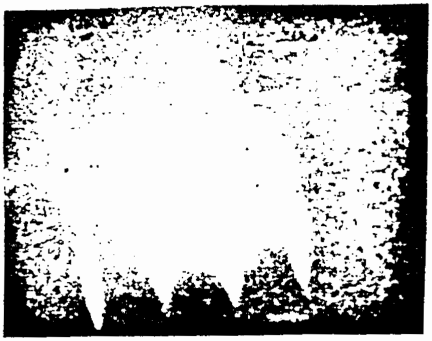

FIG 1 RHEED pattern of the CoSi$_2$ after annealing at 850°C in MBE system.

The annealing procedure is favorable for obtaining high quality CoSi$_2$ surface, since the native oxides at the surface may be desorpted at high temperature and some damage caused by sputtering may be reduced after annealing. The appearance of 2×1 reconstruction is critical for following Si overgrowth, which not only show the success of the appropriate surface treatment, but also prove the good crystalline quality of CoSi$_2$ prepared by the novel solid phase epitaxy technique. After the annealing, the substrate temperature was lowered down to 550°C. Then 100 nm thick Si was grown on the top of CoSi$_2$ at a growth rate of 0.07~0.08 nm/sec.

Fig. 2 shows the random and channeling RBS spectrum of the prepared Si/CoSi$_2$/Si structure. It shows that CoSi$_2$ is very thin with estimated thickness of about 10 nm. Because of the instrument limits, Si signal contributed from CoSi$_2$ cannot be resolved, making the determination of the atomic composition of CoSi$_2$ impossible. The reduction of Co and Si signal along channeling direction indicates the epitaxial growth of Si/CoSi$_2$/Si heterostructure. The χ_{min} of the top Si layer exhibits 59%, while that of CoSi$_2$ layer exhibits 29%. The somewhat high χ_{min} of Si signal indicates there exists some defects in the Si overlayer, which can be improved by further optimization of growth process.

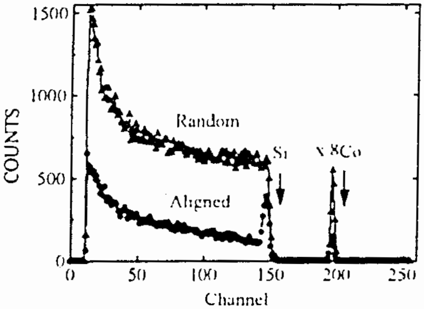

Fig 2 The random and aligned RBS spectra of the Si/CoSi$_2$/Si heterostructure.

The atomic force microscopy(AFM) shows that the 100nm Si overlayer has a surface roughness of a few nanometers. The mean roughness of Si overlayer is about 6nm.

High-resolution cross-section TEM image of the Si/CoSi$_2$/Si heterostructure along Si[110] axis shows the epitaxial characteristic as seen in Fig. 3 . The Si/CoSi$_2$/Si has following epitaxial relation:

(001)Si overlayer//(001)CoSi$_2$//(001) Si
[001] Si overlayer//[001]CoSi$_2$//[001] Si

The image shows that CoSi$_2$ has smooth interface with both Si overlayer and Si substrate. Yet there are some stacking faults and twins in Si overlayer. When carefully observed, it can be seen some stacking faults grown from the defects in CoSi$_2$.

Fig. 3(b) shows selective electron diffraction pattern of the Si overlayer along [110] zone axis. It shows the good crystalline quality of MBE-grown Si layer. Due to secondary diffraction, the (200) diffraction which is forbidden for silicon also appeared. However, it should be

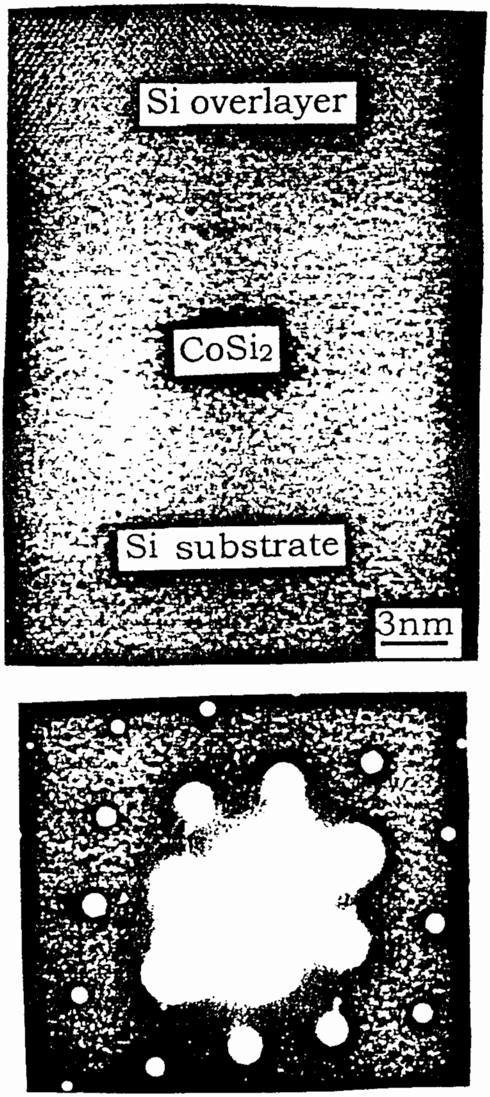

Fig.3(a). High resolution XTEM image of the Si/CoSi$_2$/Si heterostructure. (b) Selective area diffraction of Si overlayer along [110] zone axis.

pointed out that the sandwiched CoSi$_2$ layer is not homogeneous and in some region, there are some pinholes which are filled with columns of Si. In purely MBE grown purely MBE grown Si/CoSi$_2$/Si(111) system, this phenomena had also been observed, seen in Ref10. This may result from the roughness of the surface of the starting Si substrate or the thermal instability of unltra-thin CoSi$_2$ film, which could be prevented by further improving the above process.

Conclusion:

The present experiments show that the Si/CoSi$_2$/Si(100) heterostructure can be fabricated by incorporation of a novel SPE with MBE growth. A fair crystalline quality and smooth top surface of CoSi$_2$ can be obtained by Co/Ti/Si solid state reaction and subsequent proper surface treatment. Good crystalline Si can then be grown on CoSi$_2$ by MBE. RBS and TEM characterization prove the formation of the epitaxial Si/CoSi$_2$/Si heterostructure.

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