J. Indian Inst. Sci., May–June 2005, **84**, 151–156

Short Communication

Electrical properties of ion beam mixed Ti silicide at metal/Si interface

VEENU SISODIA[a,*], D. KABIRAJ[b] AND I. P. JAIN[a]
[a]Centre for Non-Conventional Energy Resources, University of Rajasthan, Jaipur 302 004, India.
[b]Nuclear Science Centre, Aruna Asaf Ali Marg, New Delhi 110 067, India.
email: mis_alt@yahoo.com, Tel. Ph. +91-141-2701602, Fax. +91-141-2710880.

Received on July 13, 2004; Revised on November 3, 2004, and March 9, 2005.

Abstract

Single-crystal *n*-Si substrates of ⟨100⟩ orientation with a metal layer Ti~18 nm have been irradiated at room temperature with ^{197}Au of 95 MeV energy. High-energy ion beam mixing has been used to obtain mixing at the interface. Titanium silicide ($TiSi_2$) formed as a result of the irradiation. The electrical properties at the interface, containing the silicide layer, the room temperature I–V curves for the pristine samples and irradiated ones have been studied. Their room temperature resistance values are estimated.

Keywords: Swift heavy ions, interface, irradiation, I–V curves.

1. Introduction

Metal silicides are widely used in very-large and ultra-large-scale integrated electronic circuits (VLSI and ULSI) as interconnects, source/drain contacts and gate electrodes. Both Ti and Co silicides are promising candidates for contacting and interconnects due to high conductivity, which lowers the sheet resistance of a shallow junction by shunting, thus decreasing the parasitic contribution to the device contact resistance [1]. Kessels *et al.* [2] have recently investigated intensely refractory metals such as W and Mo and their silicides. W and Mo act as contact materials because of some useful properties such as selective growth and high thermal stability. However, these materials have a limit to the application to ultra-large integrated circuits in the future because of high contact resistivities to Si. Today, titanium silicides are the most common choice and have been widely implemented due to low resistivity, ease of formation and self-alignment capability. In the solid-phase reaction process, titanium silicide ($TiSi_2$) is usually formed by a two-step silicidation process. First, low-temperature anneal is used to nucleate and grow the high-resistivity $TiSi_2$. After removal of the unreacted metal top layer, a subsequent high-temperature anneal is performed [3]. The system Ti/Si has been chosen because of its technological interest. The use of the technique of ion beam mixing helps in silicide formation by different mechanisms compared to that

*Author for correspondence.

formed in furnace annealing. The refractory $TiSi_2$ is the most commonly used silicide in the 0.35-*m*m generation of circuits [4]. Other crystalline titanium silicides are interesting because they are corrosion-resistive compounds. The Ti-Si system has also received interest as an amorphous alloy.

Refractory silicides (RSi_2) have high-temperature stability and high electrical conductance [5]. Low specific contact resistivities ($10^{-8}\ \Omega cm^2$) are essential to realize ULSIs, which have very small contact holes of the order of 0.1 *m*m in size [6]. Ion beam mixing is a novel technique to achieve these metal silicides. A swift heavy ion (SHI) moving at a velocity comparable to Bohr velocity can transfer energy to the material causing the modification of its properties. After the passage of SHI, the solid returns to its equilibrium state leaving behind bulk and surface modifications. Consequently, ion beams could be an ideal instrument to modify, under controlled conditions, the physical and chemical properties [7]. Leguay and Dunlop observed intermixing at Ti/Si interface as a result of 0.89 GeV Ta ion irradiation [8]. Compositional changes in Ti/Si bilayers and multilayers due to 30 KeV N_2^+ ion bombardments were studied using Auger electron spectroscopy (AES) and RBS techniques [9]. Ion beam-assisted deposition (IBAD) technique was used to achieve the formation of C54 $TiSi_2$ by direct interfacial reaction between TiSi and Si substrate [10]. The resistivity has been reported as 43.1 Ωcm for Ti and 13–16 Ωcm for $TiSi_2$ [11]. The Schottky barrier height of different metal silicides has also been an interesting field of study. It varies from 0.93 eV(IrSi) to 0.55 eV($ZrSi_2$) [12]. Schottky barrier height of Zr/Si system is 0.61 eV for *p*-type Si with boron concentration of $(1–8) \times 10^{15}\ cm^{-3}$ and 0.52 eV for *n*-type Si with phosphorous concentration of $5 \times 10^{14}–2 \times 10^{15}\ cm^{-3}$. The specific contact resistivity in Zr-*n* Si system is $3 \times 10^{-7}\ \Omega cm^{-2}$ for as-grown samples and $4 \times 10^{-8}\ \Omega cm^{-2}$ for annealed samples [13]. The role of interface states and series resistance on the I–V and C–V characteristics in MIS (metal-insulator semiconductor)-type Schottky barrier diodes have been discussed recently by Altindal *et al.* [14]. It has been explained that performance and reliability of a Schottky diode is drastically influenced by interface quality between the deposited material and the semiconductor surface. I–V studies of Ni/Si interface and SBH have also been reported recently [15]. In this paper, we present the effects of large electronic excitation and silicide formation in the Ti/Si system using the swift heavy ions (SHI) and electrical properties of the heavy ion beam intermixed Ti–Si system are discussed.

2. Experimental

A thin Ti film (~ 18 nm) was deposited on Si [100]. Top layer was Si (~ 5 nm) to avoid the oxidation of Ti. The samples were irradiated with 95 Mev Au ions at 300 K to a fluence of 10^{13} ions/cm^2, at a current of 1 pna. The electronic energy loss was found to be 20.43 keV/nm for 95 Mev Au ions in Ti by TRIM calculation**.** The structural and interfacial properties of Ti/Si interfaces have been investigated using the Rutherford backscattering spectroscopy (RBS), X-ray reflectivity (XRR) and Grazing angle X-ray diffraction (GIXRD). The RBS simulation using the RUMP [16] shows the mixing in a zone, which is 20–25 Å thick. RBS spectra are shown in Fig. 1. In GIXRD curves, sharp crystalline peaks appear as a result of irradiation, which can be identified to be crystalline $TiSi_2$ phase as shown in Fig. 2. Thus, characterization of the samples by X-ray diffraction and RBS of the samples confirms mixing at the interface. Details of the mechanism of silicide formation in

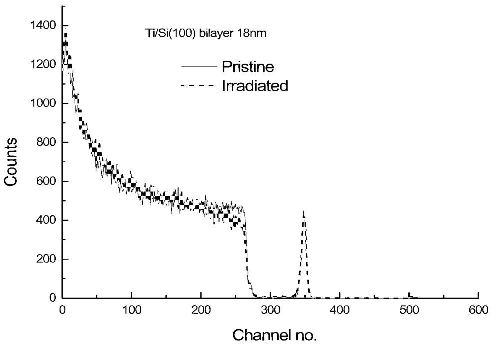

FIG. 1. RBS spectra of pristine and Au ion (95 MeV)-irradiated Ti/Si specimen.

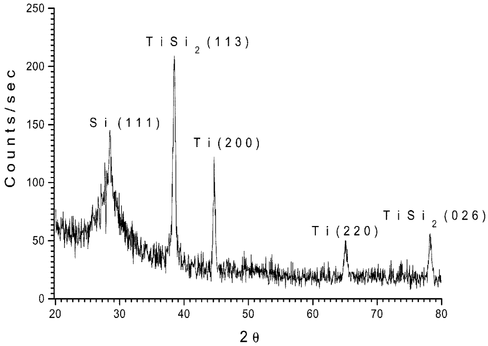

FIG. 2. GIXRD spectra of Au ion (95 MeV)-irradiated Ti/Si specimen.

the system are discussed in our earlier paper [17]. After mixing, investigation of the electrical properties at the interface is done to infer the interface states. For electrical measurements silver paint was applied for the top and bottom contacts in the specimen. I–V characteristics measurements were taken in the vacuum of the order of 10^{-5} Torr using electrometer (Keithley Electrometer Model 610-c).

2.1 *Electrical measurements*

From electrical measurements we can infer the presence of surface states. If they are present, the barrier height can be determined by the interface states and these states are due to the interfacial layer between silicon and silicide. The position of these interface states is determined by the kind of metal and their density can depend upon the interfacial composition. The fact that changing the kind of composition does not change the value of SBH simply means that that even if the interfacial layer changes, the corresponding changes in the density of states is not enough to produce an appreciable effect on the position of the fermi level. Thus, an interfacial layer having a composition different from pure metal or silicon or compound seems to be responsible for the main features observed in the metal-silicon interactions and electrical contacts [18].

2.2 *I–V characteristics*

I–V characteristics have been measured for as-deposited and irradiated samples. I–V methods were then used to measure the Schottky barrier height of the samples. Figure 3 shows the room-temperature I–V characteristics of different samples. It is observed that the samples that were subjected to irradiation shift towards linearity in comparison to the pristine ones. For Ti/Si samples the room temperature resistances of the pristine and irradiated ones have been calculated as 241 and 200 Ω, respectively. Thus in different samples there is a decrease of ~20% or more in the contact resistivity of the sample. The resistivity plot is shown in Fig. 4 and is in accordance with the literature. For the irradiated samples this decrease may be attributed to the generation of radiation-induced defect states energy gap and compensates the free carriers in the substrate. Thus it is a result of SHI-induced silicide formation at the interface, which is also confirmed from the X-ray studies.

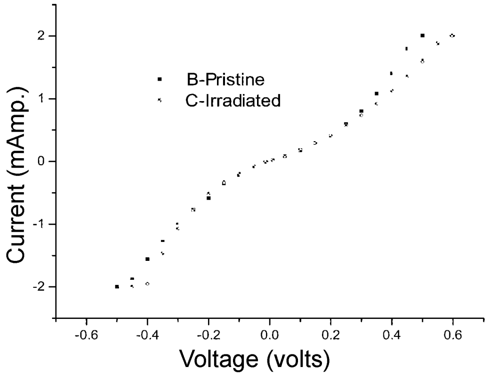

FIG. 3. I-V characteristics of pristine and Au ion (95 MeV)-irradiated Ti-Si specimen.

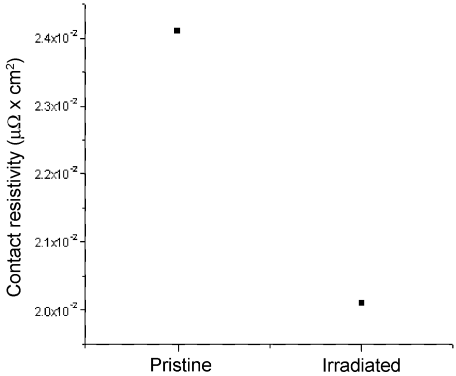

FIG. 4. Resistivity plot of Ti-Si samples before and after Au ion (95 MeV) irradiation.

2.3 *Schottky barrier height*

Barrier height is one of the most important parameters of the Schottky barrier diodes. In a reactive interface such as silicide–Si interface there is an interfacial region, which tends to dominate the Schottky barrier height. The layer should control not only the barrier height, but also other interfacial properties as well. Here we will discuss the barrier height of Ti-*n* Si diode by variation of zero bias barrier height and ideality factor for such a diode. For a Schottky barrier diode, the relation between the applied forward bias and current of the device is due to the thermionic emission current and it can be written as

$$I = I_o[\exp(qv/nkt) - 1]$$

where n is the ideality factor, I_o, the saturation current and defined by

$$I = AA^*T^2\exp(-q\Phi_{B0}/KT)$$

where the quantities A, A^*, T, q, k and Φ_{B0} are, respectively, the diode area, the effective Richardson constant, $T = 300$ K is the measurement temperature, the electronic charge, Boltzmann's constant and apparent barrier height. The I_o was obtained by extrapolating the linear region of the curve to zero applied voltage and the Φ_{B0} values were calculated from the second equation. The values of ideality factor n were obtained from the slope of linear region of the I–V plots. Nevertheless, it is the interfacial region that dominates the Schottky barrier formed. In turn, all the features are determined by the strength and nature of interfacial bonding of formation [19]. There will be reaction-driven diffusion across the interface once reaction is initiated. The barrier height Φ_B of Ti-*n* Si interface is calculated from the I-V curves of different specimens.

Sample kind	SBH
Pristine	–0.46 eV
Irradiated	–0.78 eV

The precise composition at the Si interface in the Ti/Si interface is always close to $TiSi_2$ over Si after irradiation. Hence, the Φ_B depends on the crystallinity of the $TiSi_2$ at the Si interface, not on the composition of Ti-Si alloy. It has been reported that the barrier height does not change as the interdiffused amorphous Ti-Si alloy thickness increases [20] and this result supports the suggestion that the interface is critical for the barrier height.

2.4 *Chemical dependence of Schottky barrier height*

Experiments carried out under UHV conditions have shown that intrinsic surface states are not present in the bandgap of the most compound semiconductors for clean, well-cleaved surfaces and therefore play no role in the Schottky barrier process [21]. Instead, chemical reaction and interdiffusion between the metal and the semiconductor are found to play a dominant role. Such chemical phenomenon leads to a new picture of the Schottky barrier junction. In contrast to the sharp boundary between metal and semiconductor, the interface in general encompasses an extended region and may involve a reacted region with new dielectric properties and chemical compositions. In a reactive interface such as silicide-Si interfaces there is an interfacial layer which tends to dominate the Schottky barrier height. This interface layer is a reacted layer of two solids in contact.

Acknowledgement

The authors thank the Nuclear Science Centre (NSC), New Delhi, India, for sample preparation and irradiation part of the experiment. NSC also supported VS with financial assistance in the form of Junior Research Fellowship. Sincere thanks are due to IIT, Kanpur, India, for the RBS facility and to XRD Lab, Solid State Physics Laboratory (SSPL) India, for X-ray analysis.

References

1. K. Maex, Silicides for integrated circuits:$TiSi_2$. $CoSi_2$, *Mater. Sci. Engng Rep.*, **11**, 53–57 (1993).
2. M. J. H. Kessels, J. verhoeven, A. E. Yaskin and F. Bijkerk, Ion beam induced intermixing of interface structures in W/Si multilayers, *Nucl. Instr. Meth. B*, **222**, 484–490 (2004).
3. K. K. Larsen, F. A. Via, S. Lombrado, V. Raineri, R. A. Donaton and S. U. Campisano, Ti silicide and secondary defect annihilation in ion beam processed SiGe layers, *Mater. Res. Soc. Symp. Proc.*, **402**, 149–154 (1996).
4. S. P. Morarka, *Silicides for VLSI applications*, Academic Press, pp. 30, 51, 130, 200 (1983).
5. M. Ekman and V. Ozolins, Electronic structure and bonding properties of titanium silicides, *Phys. Rev. B*, **57**, 4419–4424 (1998).
6. T. Yamauchi, S. Zaima, K. Mizuno, H. Kitamura, Y. Koide and Y. Yasuda, Solid phase reaction and crystallographic structures in Zr/Si system, *J. Appl. Phys.*, **69**, 7050–7056 (1991).
7. M. Toulemonde, C. Trautmann, E. Balanazt, K. Hjort and A. Weidinger, Track formation and fabrication of nanostructures with MeV-ion beams, *Nucl. Instr. Meths. Phys. Res. B*, **216**, 1–8 (2004).
8. R. Leguay and A. Dunlop, Evidence for atomic mixing induced in metallic bilayers by electronic energy deposition, *Nucl. Instr. Meth. B*, **122**, 481–502 (1997).
9. M. Bonelli and K. Roger, Compositional changes in N_2^+ bombarded Ti/Si bilayers and multilayers: Interplay between random and chemically guided effects. *Nucl. Instr. Meth. B*, **127/128**, 102 (1997).
10. J. Chang, G. B. Kim, D. Yoon and H. Baik, Investigations of the mechanism of titanium silicide using ion beam assisted deposition, *Appl. Phys. Lett.*, **75**, 2900–2902 (1999).

11. M. A. Nicolet and S. S. Lau in *VLSI electronics* (N. G. Einspruch and G. B. Larrabe, eds), Vol. 6, p. 523, Academic Press (1983).
12. R. T. Tung, J. M. Gibson and J. M. Poate, Chemical bonding and Schottky barrier height of silicides, *Phys. Rev. Lett.*, **50**, 429–432 (1983).
13. T. Yamauchi, S. Zaima, K. Mizumo, H. Kitamura, Y. Koide and Y. Yasuda, Solid phase reaction and electrical properties in Zr/Si system, *Appl. Phys. Lett.*, **57**, 1105–1107 (1990).
14. S. Altindal, S. Karandeniz, N. Tuðluoðlu and A. Tataroðlu, The role of interface states and series resistance on the I-V and C-V characteristics in Al/SnO_2/*p*-Si schottky diodes, *Solid St. Electronics*, **47**, 1847–1854 (2003).
15. V. Sisodia, D. Kabiraj and I. P. Jain, Schottky barrier height measurement of swift heavy ion intermixed Ni-silicide interface, *Nucl. Instr. Meth. B*, **222**, 256–260 (2004).
16. Doolittle *et al*., *RBS simulation software*, 1985, 1986.
17. V. Sisodia, R. K. Jain, D. Bhattacharya, D. Kabiraj and I. P. Jain, Structural modifications by swift heavy ions at metal/silicon interface, *Radiation Measurements*, **36**, 657–661 (2003).
18. G. Ottaviani, Interface metallurgy and electronic properties of silicides, *J. Vac. Sci. Technol*., **18**, 924–928 (1981).
19. L. J. Brillson and C. F. Brucker, New method for control of Schottky barrier height, *Appl. Phys. Lett.*, **39**, 67–69 (1981).
20. M. Giudice, J. J. Joyce, M. W. Ruckman and J. H. Weaver, Silicide formation at the Ti/Si [111] interface: Room temperature reaction and Schottky barrier formation, *Phys. Rev. B*, **35**, 6213–6217 (1987).
21. J. V. Larr and A. Huijser, Interface chemistry and Schottky barrier height at Ni/Si interface, *J. Vac. Sci. Technol*., **13**, 769–774 (1976).