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Structural and optical characterization of Ru_2Si_3 layers on Si formed by a two-step channeled ion implantation

ChangChun Chen[a],*, BenHai Yu[b] and JiangFeng Liu[b]
[a]*College of Materials Science and Engineering, Nanjing University of Technology, NO.5 Xinmofan Road, Nanjing 210009, China*
[b]*College of Physics & Electronic Engineering, Xinyang Normal University, Henan Province, 464000, China*

Structural and optical properties have been investigated for Ru_2Si_3 layers on Si (100) formed by two-step channeled ion implantations (70 keV, $6.92 \times 10^{16}/cm^2$ and 40 keV, $4.31 \times 10^{16}/cm^2$) and subsequent annealing at 1150 °C for 120 second. Rutherford backscattering/ ion channeling (RBS/C) analyses have revealed that the Ru_2Si_3 layers were grown on the Si substrate but with a rather poor crystalline quality. The optical spectra have been obtained by spectroscopic ellipsometry (SE) and optical absorption measurements. From the optical investigations, the real and imaginary parts of the dielectric function as well as the absorption coefficient have been derived. The spectra of Ru_2Si_3 layers exhibit a semi-conducting character with an allowed direct band gap of 0.843 eV.

Key words: Ru_2Si_3, Channeled ion implantation, spectroscopic ellipsometry (SE), optical properties.

Introduction

In recent years much effort has been devoted to obtain silicon-based light-emitting devices [1-2]. One of the several approaches towards this goal is the use of semiconducting silicides to modify their band-gap structures. Among them, orthorhombic ruthenium silicide (Ru_2Si_3) is an interesting semi-conducting silicide predicted to have a direct band-gap smaller than that of Si [3]. According to theoretical and computational analyses, the band-gap of ruthenium silicide is around 0.45 eV, however some authors demonstrated that the actual band gap may be between 0.7 eV and 1.09 eV [4]. The results on the band gap value suggest that light emission from an orthorhombic Ru_2Si_3 is expected in the near-infrared and Ru_2Si_3 is a very promising silicon-based light-emitting material. So far, four different techniques have been used to grow Ru_2Si_3 film on silicon: (i) high energy implantation of Ru^+ ions in silicon followed by high temperature re-crystallization and silicidation [5]; (ii) deposition of thin Ru films on silicon and growth of Ru_2Si_3 via a solid state reaction at elevated temperatures; (iii) a molecular beam epitaxial (MBE) reaction by co-deposition of Ru and Si on Si [4]; (iv) sputtering from ruthenium or ruthenium silicide targets with subsequent annealing in the temperature range of 400-800 °C [6]. However, only approaches (ii) and (iii) can realize the epitaxial growth of Ru_2Si_3 films on Si and the Ru_2Si_3 films fabricated by ion beam synthesis or sputtering are merely polycrystalline structures.

*Corresponding author:
Tel : +8602583587242
Fax: +8602583587242
E-mail: changchunchen@hotmail.com

In this paper, we have fabricated ruthenium silicide (Ru_2Si_3) layers on Si (100) substrate by a two-step channeled ion beam synthesis (CIBS) method utilizing the benefits of channeled ion beam implantation, such as the smaller sputtering yield, lower defect density, etc [7-8]. The structural and optical properties of the Ru_2Si_3 layers have been thoroughly investigated by RBS/C, SE and optical absorption measurement.

Experimental

The Ru_2Si_3 layers were produced by two-step implantation of Ru^+ ions into Si (100) substrates along the [100] axis of the Si substrate followed by a rapid thermal annealing. Ruthenium chlorides were used in a Nielsen plasma ion source to produce the Ru^+ ions. Si (100) substrates were first implanted with 70 keV Ru^+ ions to a fluence of $6.92 \times 10^{16}/cm^2$, followed by implantation of 40 keV Ru^+ ions to a fluence of $4.31 \times 10^{16}/cm^2$ at 300 °C with the aim of allowing dynamic annealing, thereby minimizing implantation damage. The ion beam current was approximately 3-5 μA. During implantation, the Ru^+ ion beams were directed within ± 1.5° of the [100] axis of the Si substrate to maintain the channeled implantation conditions. The as-implanted sample was cut into two parts and one of them was subsequently annealed at 1150 °C for 120 seconds in a rapid thermal furnace under a N_2 atmosphere. For simplicity, the sample annealed at 1150 °C for 120 seconds is referred to as the annealed sample. It is worth noting that the two-step implantations of 70 keV Ru^+ ions to a fluence of $6.92 \times 10^{16}/cm^2$ and 40 keV Ru^+ ions to a fluence of $4.31 \times 10^{16}/cm^2$ used in this study are aimed at obtaining a continuously implantation layer. Under these implantation conditions, the depth profiles

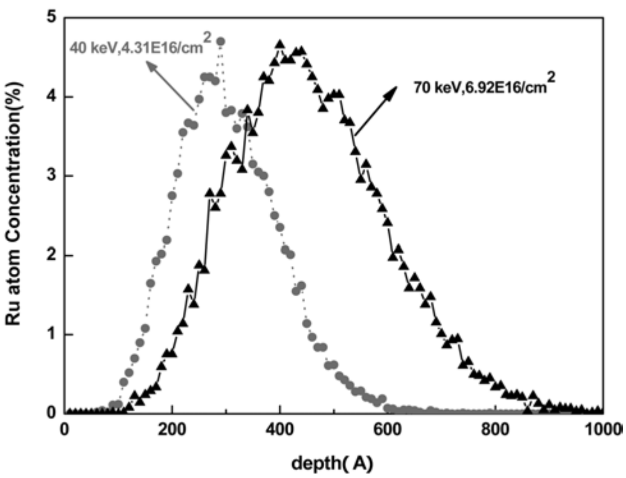

Fig. 1. The depth profile of Ru^+ ions in the Si substrate implanted by a two-step CIBS.

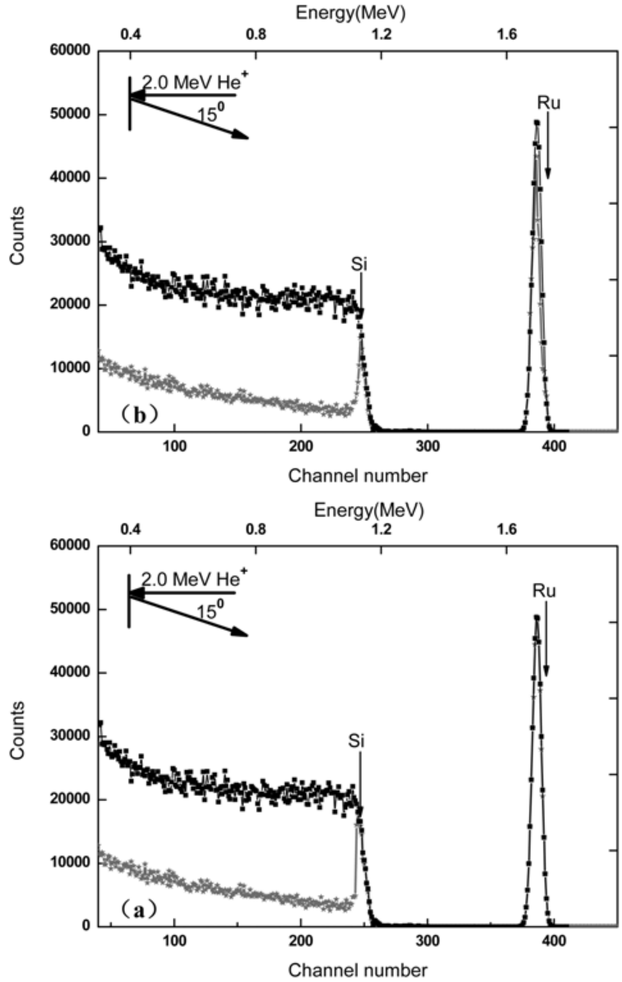

Fig. 2. Random and aligned RBS spectra of the as-implanted sample (a) and the annealed sample (b) with Ru^+ ions implanted under channeling conditions.

of Ru^+ ions in the Si substrate calculated using the SRIM-2003 program are shown in Fig. 1 [9]. The chemical composition, thickness and crystalline characteristics of both the as-implanted and the annealed samples were determined by Rutherford backscattering/ ion channeling (RBS/C). RBS/C was carried out using 2.0 MeV $^4He^+$ ions at a scattering angle of 165° and at normal incidence using a standard Au-Si surface barrier detector with an energy resolution of 18 keV full-width at half-maximum (FWHM). The analysis of RBS random spectra was carried out using the SIMNRA program [10]. Room temperature ellipsometric measurements were carried out by a variable angle of incidence spectroscopic ellipsometry (SOPRA, France). Room temperature (RT) optical absorption measurements were performed to determine the absorption coefficient (a) and the bandgap energy (E_g). The optical absorption measurements were carried out in Peking University, in transmission mode, using a tungsten lamp as a white light source, a quarter meter spectrometer and a liquid-nitrogen cooled germanium detector to monitor the transmitted light. The method used in this study was the same as that described in more detail previously [11].

Results and Discussion

The RBS/channeling spectra of the as-implanted and the annealed sample are presented in Figs. 2(a) and (b), respectively. The arrows (labeled Si, and Ru) indicate the backscattering energy from these elements at the surface. The structural characteristics of these two samples can be determined from the random spectrum while the crystallinity can be obtained from the channeling spectrum. Since the minimum yield from only the element with the largest atomic weight in a polyatomic crystal indicates the crystal quality [12], we used χ_{Ru} as an indicator of crystalline perfection. The implanted fluence of Ru ions for the as-implanted sample from the random spectrum shown in Fig. 2(a) were calculated as $9.61 \times 10^{16}/cm^2$. The calculated values of Ru^+ ion fluence in the Si substrate below the implanted fluence are likely attributed to the implantation loss. In addition, the χ_{Ru} obtained from the Ru part of the aligned spectrum (shown in Fig. 2(a)) is 1.0 showing a very high defect density for Ru^+ ion implantation. The thickness and the Ru: Si ratio obtained from the random spectrum of the annealed sample using the SIMNRA program [13] (shown in Fig. 2(b)) were about 80.2 nm, and 2 : 3, respectively. The aligned spectrum in Fig. 2(b) reveals that the χ_{Ru} value of the Ru peak was about 89.3%, showing that the Ru_2Si_3 was grown on the Si substrate but with a rather poor crystalline quality. As pointed out by Sharpe *et al*. [14], when implantation conditions were improved, the polycrystalline Ru_2Si_3 nature of the silicon matrix could be obtained with a significant improvement in maintaining the crystallinity. Therefore, in this study, although the Ru_2Si_3 layer could be demonstrated to grow on the Si (100) wafer, the implantation and annealing conditions, such as the Ru^+ ion current density, the substrate temperature, and the thermal budget will be further optimized to form a Ru_2Si_3 layer with good crystalline quality.

The real and imaginary parts of the dielectric constant

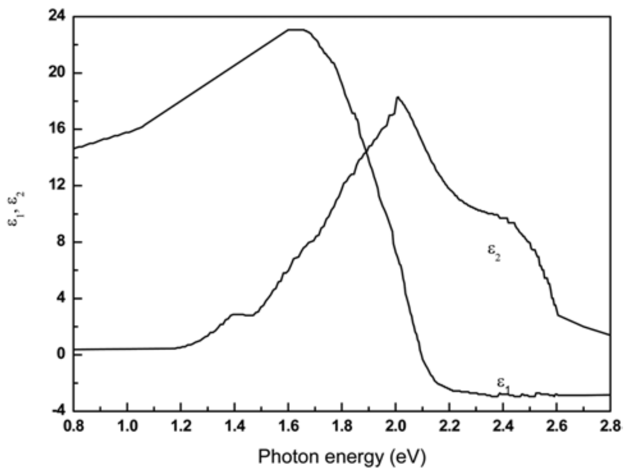

Fig. 3. Real (e_1) and imaginary (e_2) part of the dielectric function of Ru_2Si_3 obtained by a two-step channeled ion implantation for the annealed sample.

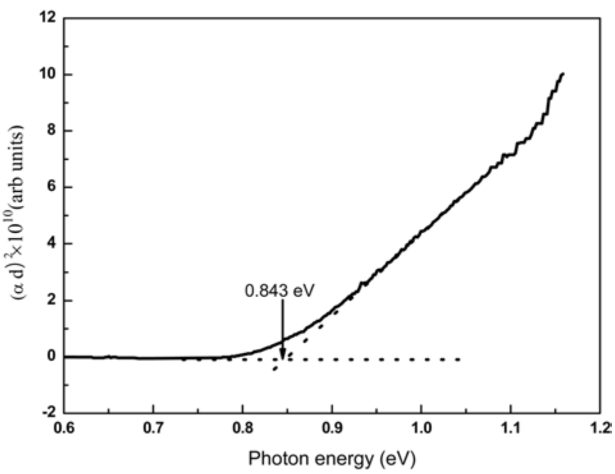

Fig. 4. Values of the squared absorption coefficient (a) times the thickness (d) of the Ru_2Si_3 layer for the annealed sample measured at room temperature as a function of photon energy.

determined from the room temperature ellipsometric spectra of the annealed sample are presented in Fig. 3. The spectral shapes of ε_1 and ε_2 are very similar to those of other semi-conducting silicides [15]. In addition, the imaginary part of the dielectric constant of the Ru_2Si_3 layer has a peak around approximately 2.0 eV and decays rapidly at lower photonic energies, which is similar to the reports by other research groups [4]. The peak at 2.0 eV corresponds with the fact that for nearly all 3d transition metal silicides peaks are found in the region between 1.0 and 2.0 eV. Consequently, the ellipsometric measurements shown in Fig. 3 demonstrate that a semi-conducting silicide formed by a two-step channeled ion implantation followed by high temperature annealing could be obtained.

The optical band gap at room temperature was investigated by optical absorption measurements. As is known, the nature of a band gap transition can be revealed by the relation of the absorption coefficient a versus photon energy hn. For a direct transition, $\alpha(h\nu)$ is equal to, $A(h\nu - E_g^d)$ however, $\alpha(h\nu)$ is equal to $A^*(h\nu - E_g^{ind} - E_{ph})$ for an indirect transition, where E_g^d and E_g^{ind} are the direct and indirect band gaps, respectively, and A and A^* are constants depending on the details of the band structure and E_{ph} is the phonon energy [16]. Values of the square of a multiplied by the thickness (d) of the Ru_2Si_3 layers are shown as a function of photon energy for the annealed sample in Fig. 4. The linear fit of the curve indicates that the Ru_2Si_3 layer has an allowed direct energy gap. On the other hand, from linear extrapolation of the linear portions to $(a \times d)^2 = 0$, the room temperature value of the direct band gap was deduced to be 0.843 eV for the Ru_2Si_3 layer. This value is in good agreement with previous reports [17]. At the same time, extrapolation of the ellipsometric spectrum (shown in Fig. 3) of the squared imaginary part of the dielectric function e_2 also could also yield a value of 0.841 eV for for the Ru_2Si_3 layer. The band gap values obtained from ellipsometric and optical absorption measurement were in a good agreement.

Conclusions

The growth of ruthenium silicides on a silicon wafer using a two-step CIBS and followed by high temperature annealing was investigated. RBS/C experiment demonstrated that the ruthenium silicide layer was Ru_2Si_3 and it could be gown on a Si substrate with rather poor crystalline quality. Both the ellipsometric and optical absorption measurements at room temperature have revealed that the Ru_2Si_3 layer exhibited a semi-conducting character with an allowed direct band gap of 0.843 eV.

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