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ABSTRACT

High doses (10^{16}–10^{17}/cm^2) of 170 keV Er$^+$ were implanted into single-crystal ⟨111⟩ Si at implantation temperatures between 350°C and 520°C. Annealing at 800°C in vacuum following the implant, the growth and coalescence of $ErSi_2$ precipitates leads to a buried single crystalline $ErSi_2$ layer. This has been studied using Rutherford backscattering/channeling, X-ray diffraction, cross-sectional TEM and resistance versus temperature measurements. Samples implanted at 520°C using an Er dose of 7×10^{16}/cm^2 and thermally annealed were subsequently used as seeds for the mesoepitaxial growth of the buried layer during a second implantation and annealing process. Growth occurs meso-epitaxially along both interfaces through beam induced, defect mediated mobility of Er atoms. The crystalline quality of the $ErSi_2$ layer strongly depends on the temperature during the second implantation.

INTRODUCTION

One of the interesting features of the rare earth silicides is that they form the lowest known Schottky barrier heights on n-type Si [1,2] and appear to be potentially attractive as low contact resistance materials for high integration density device structures. Until now, most investigations have involved interaction of deposited rare-earth thin films with single crystal Si. Silicides of Tb, Ho, Er, Tm, Yb, Lu, and Y have been shown to grow by solid phase epitaxy [3,4] while silicides of Tm, Yb, Lu, Gd, and Dy can be formed epitaxially in liquid phase reaction using electron beam melting. Single crystal $ErSi_2$ layers have also been formed using ultrahigh vacuum co-deposition of Er and Si followed by an appropriate thermal annealing [5,6]. While there are convincing demonstrations of the utility of ion beam synthesis in the formation of transition metal silicides [7 and ref. therein], only a few results concerning ion beam synthesis of rare earth silicides have been reported so far [8], possibly reflecting the potential difficulties related to the high theoretical value of the sputtering coefficient which may act as a dose-limiting factor for rare earth ions. It has been recently shown, however, that ion implantation at elevated temperatures followed by an appropriate thermal annealing may be used to synthesize single crystalline erbium di-silicide [9]. It has also been shown [9] that at implantation temperature $T_i > 280$°C, the morphology of Er implanted Si is strongly influenced by two ion beam induced phenomena. Firstly, the defect mediated diffusion of erbium occurring at temperatures at least 400°C below the minimum temperature required for the thermally activated Er diffusion to become observable. Secondly, the ion beam induced formation of the polycrystalline $ErSi_2$ phase occurring at $T_i > 280$°C, at least 100°C below the temperature required for contact reactions between a Si substrate and deposited Er metal to occur.

The goal of the present work has been to answer the question of whether or not ion beam induced phenomena may contribute to the mesotaxial growth of the single-crystalline di-silicide layer during Er ion implantation at low temperatures.

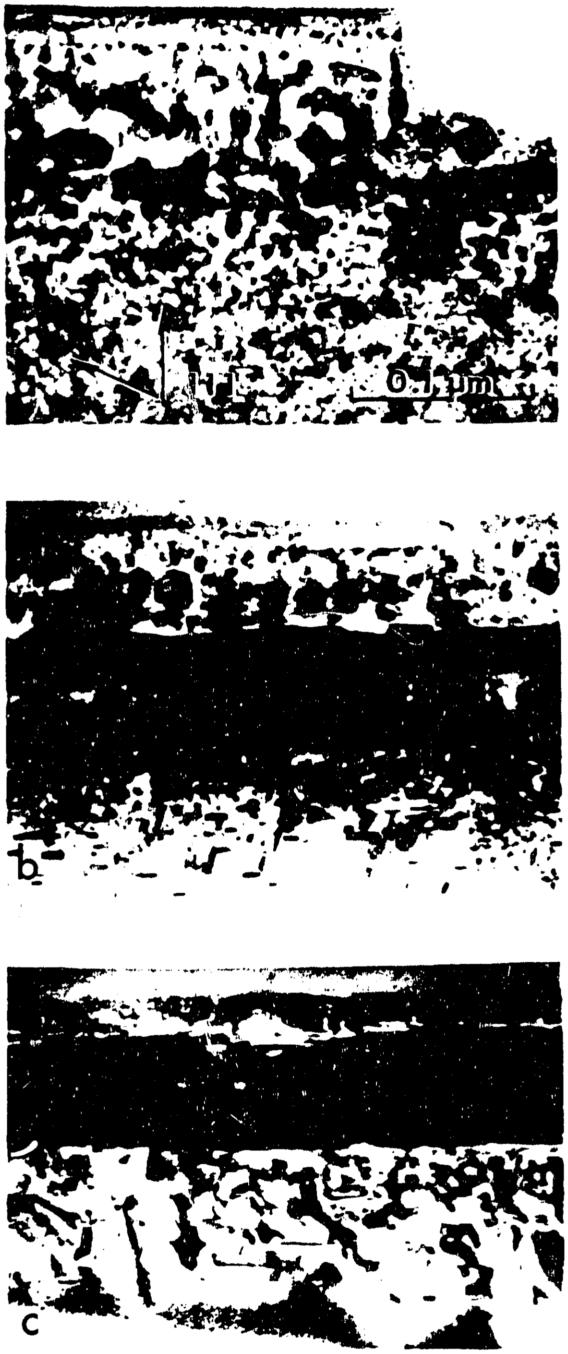
EXPERIMENTAL

170 KeV Er^+ ions, produced using a sputter ion source were implanted into (111) oriented single-crystal Si. Careful precautions were taken in order to minimize channeling effects during implantation. The substrate temperature T_i was regulated within the range RT < T_i < 520°C using a heater located within the sample holder. The ion beam current density was maintained below 10 $\mu a/cm^2$. Implanted samples were annealed under vacuum (8×10^{-7} Torr). Isochronal (1h) and isothermal (700°C) annealings were carried out in order to estimate the value of the activation energy E_a for $ErSi_2$ phase formation. The implanted samples were routinely annealed in two steps at 650 and 800°C. The samples implanted at 520°C using an Er^+ dose of 7×10^{16} cm^2 and thermally annealed were subsequently used as seeds for mesotaxial growth. They were reimplanted using various doses of 170 keV Er^+ ions at 250 < T_i < 520°C, and reannealed at 800°C. Rutherford backscattering – ion channeling analysis (RBS) using 1.2 MeV He ions, cross-sectional transmission electron microscopy (XTEM) and resistance versus temperature measurements were used to characterize the implanted and annealed samples.

RESULTS AND DISCUSSION

Formation of the Single Crystal Di-Silicide Phase

High dose implantation of Er into single crystal (111) Si at elevated implantation temperatures (T_i > 280°C) has been shown to result in the formation of the polycrystalline $ErSi_2$ phase [9]. This leads to an increase in the surface binding energy, causing a 30% decrease in the sputtering coefficient and a similar increase in the retention of Er. For T_i > 400°C, the $ErSi_2$ crystallizes as coherent precipitates within a crystalline Si matrix (Fig. 1a). During subsequent thermal annealing, the Er distribution narrows due to Ostwald ripening [10], and a buried layer of single-crystalline $ErSi_2$ is formed (Fig. 1b) [9]. The transformation of the Er implanted system occurring during the annealing process is shown in Fig. 2. The RBS/channeling spectra shown correspond to the (111) Si sample implanted at T_i = 520°C, using $8 \times 10^{16}/cm^2$, 170 keV Er^+ ions, and subsequently annealed using a two-step annealing at 650 and 800°C. A temperature of 800°C appears to be the optimum annealing temperature as higher temperatures lead to an increase in the dechanneling yield and a broadening of the Er distribution.



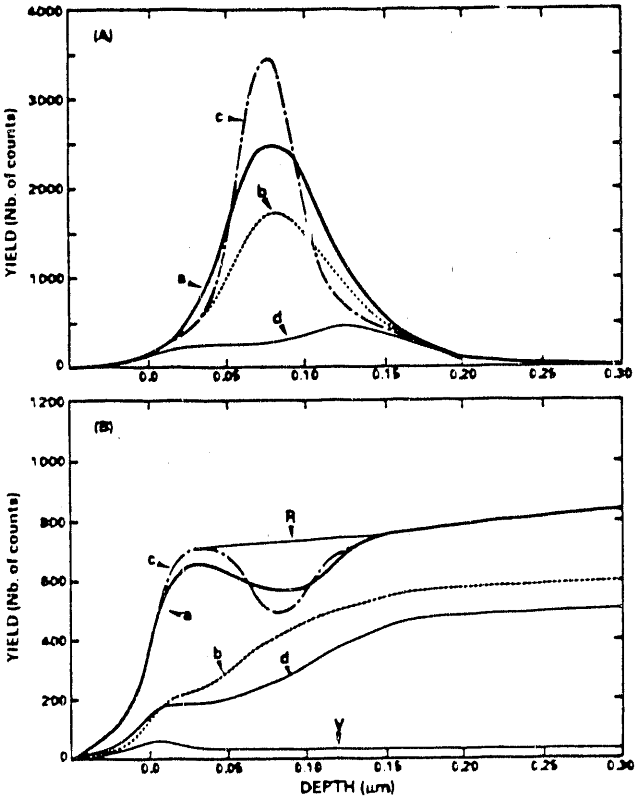


Fig. 1. Cross-section TEM micrographs from Er (170 keV, 8 × 10^{16}/cm², 520°C) implanted Si (111): (a) as-implanted, (b) following [illegible] annealing, and (c) following sequential implantation and annealing as described in text.

Fig. 2. Ion beam synthesis of the single crystal $ErSi_2$ phase: RBS/channeling spectra for Er (A) and Si substrate (B), corresponding to the ⟨111⟩ Si sample implanted with Er^+ (170 keV, $8 \times 10^{16}/cm^2$) at $T_i = 520°C$ and subsequently thermally annealed under vacuum, as implanted (a) random, (b) aligned and after annealing, (c) random, and d) aligned. R and V denote random and aligned spectra from virgin Si.

In order to obtain an estimate of the activation energy for the di-silicide formation occurring during thermal annealing, isothermal (700°C) and isochronal [illegible] were carried out and the remaining fraction of interstitial Er atoms was subsequently measured using the RBS/channeling technique.

We have attempted to fit the theoretical predictions of the Waite's rate equation [11] to our data using the activation energy E_a as the fitting parameter. The resulting best fit value is $E_a = 3.6$ eV. The corresponding diffusion length calculated for a diffusion time of 0.5 h at 350°C is close to 1 Å, consistent with our earlier reported observation that the mobility of Er atoms occurring during Er implantation at T_i close to 350°C [9] is related to beam induced effects, and cannot be understood on the basis of a simple thermal diffusion process.

We also note that as one might expect the value of 3.6 eV is considerably higher than the earlier reported $E_a = 2.5$ eV for $CoSi_2$ formation by Co diffusion [12].

Ion Beam Induced Mesotaxial Growth of Buried Di-Silicide Layer

A series of similar samples containing buried layers of single-crystalline $ErSi_2$ was prepared for use as seeds. In order to investigate the mesoepitaxial growth of the single crystalline di-silicide phase occurring during Er implantation, the seed samples were subsequently reimplanted with 170 keV Er ions at $250 < T_i < 520$°C. The ion beam current density was maintained below 10 $\mu A/cm^2$. The mesotaxial growth occurring during the reimplantation process is shown in Fig. 3. The buried $ErSi_2$ layer grows mesotaxially along both interfaces. The final positions of the lower and upper interfaces depend on the implanted dose. The growth rate is similar on both sides of the seed and remains approximately constant for the doses used in this experiment.

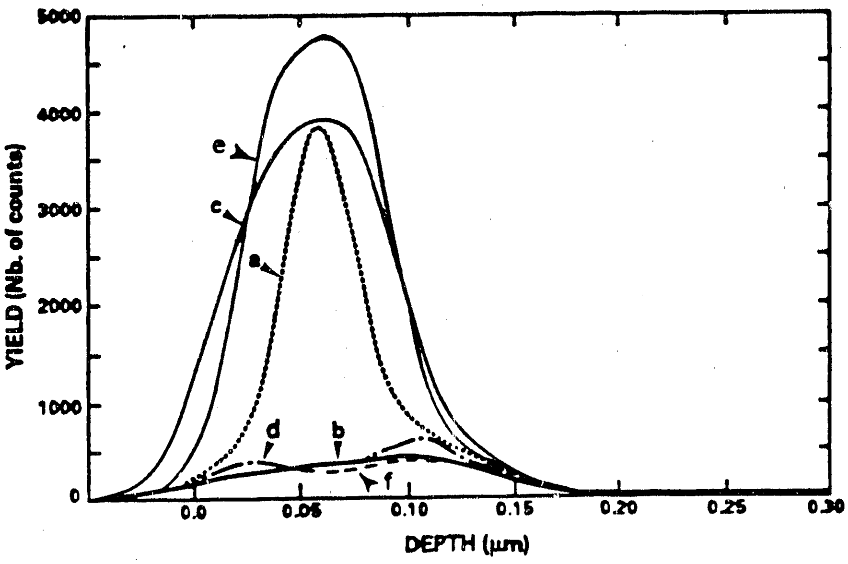


Fig. 3. Mesotaxial growth of a seed sample occurring during reimplantation of 6×10^{16} cm^2 at 520°C showing random and aligned RBS spectra respectively from the seed (a,b), after the second implantation (c,d) and after a second anneal at 800°C (e,f).

These samples were subsequently reannealed at 800°C. The RBS/channeling spectra and the XTEM micrograph corresponding to the second implantation-annealing sequence are shown in Figs. 3 and 1(c), respectively. It is clearly seen that during the second thermal annealing, the Er distribution narrows again. For the total dose of 1.3 × $10^{17}/cm^2$, the average stoichiometry of the buried layer becomes close to $ErSi_{2.5}$, indicating that during the second sequence the amount of Si bridging the gaps between the di-silicide islands decreased by ~25%. Interestingly, the buried di-silicide layer remains discontinuous. This is consistent with the results of the electrical measurements shown in Fig. 4. The normalized resistance versus temperature dependence for the Er doses of 7 × $10^{16}/cm^2$ (a) and 1 × $10^{17}/cm^2$ (b) are compared to the curve (c) corresponding to the $ErSi_2$ layer formed using ultrahigh vacuum codeposition of Er and Si followed by an appropriate thermal annealing [5,6]. The shape of the curves (a) and (b) strongly suggests that the observed conductivity of the system represents a convolution of the metallic and semiconductor type conductivities. This is attributed to the fact that the buried di-silicide layer is discontinuous. A curve of similar shape (not shown) has also been obtained for the total Er dose of 1.3 × $10^{17}/cm^2$. The persistence of the anomaly observed in the vicinity of 150 K indicates that the gaps between the di-silicide islands cannot be bridged for the Er doses used in this work. We conclude that the mesotaxial growth of the $ErSi_2$ phase is strongly orientation-dependent.

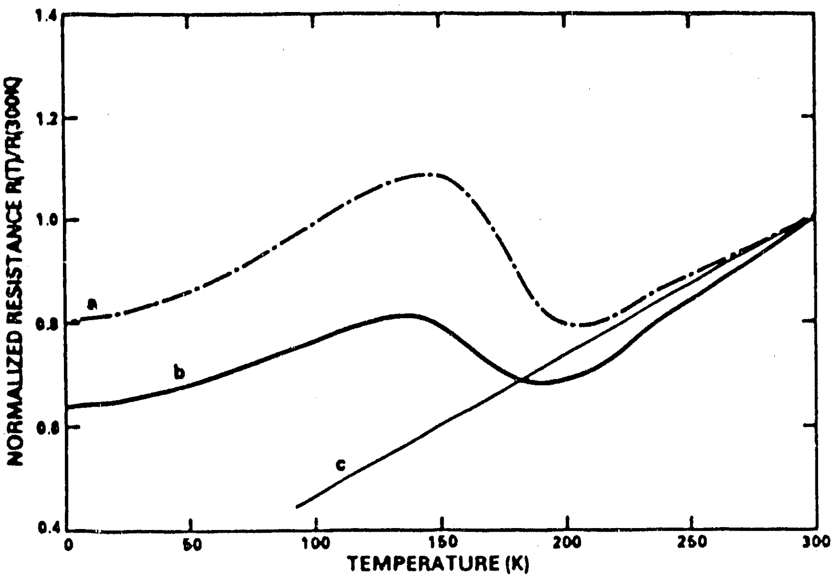


Fig. 4. Normalized resistance versus temperature curves for buried $ErSi_2$ layers formed using 170 keV Er ion doses of 7 × $10^{16}/cm^2$ (a) and 1 × $10^{16}/cm^2$ (b). Curve (c) corresponding to the $ErSi_2$ layer formed using ultrahigh vacuum codeposition of Er and Si followed by an appropriate thermal annealing [5,6] is shown for comparison.

The RBS/channeling technique has also been used to compare the quality of the buried di-silicide layers formed using either sequential or single-step processing. For the total implanted dose of 1 × $10^{17}/cm^2$ the Xmin values corresponding to the erbium peak (not normalized with respect to the dechanneling occurring within the Si matrix) are equal to 23% and 14% for the single-step processing and sequential processing, respectively.

CONCLUSIONS

1. We have provided experimental evidence that single crystal erbium di-silicide may be formed via ion beam synthesis using Er implantation at elevated temperatures followed by an appropriate thermal treatment. The activation energy for the single-crystalline $ErSi_2$ phase formation is close to 3.6 eV.

2. We have shown for the first time that the mesotaxial growth of the single crystalline Er di-silicide phase occurs during Er implantation at implantation temperatures $T_i > 300°C$. The mechanism of the growth is shown to be related to the ion beam-induced, defect mediated diffusion of Er atoms.

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