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<td>Tan, Eu Jin; Pey, Kin Leong; Chi, Dong Zhi; Lee, Pooi See; Setiawan, Y.; Hoe, Keat Mun</td>
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Materials and Electrical Characterization of $\text{Er} (\text{Si}_{1-x} \text{Ge}_x)_{2-y}$ Films Formed on $\text{Si}_{1-x} \text{Ge}_x (001) \ (x = 0–0.3)$ via Rapid Thermal Annealing

E. J. Tan$^{a,b,d,z}$ K. L. Pey$^a$ D. Z. Chi$^b$ P. S. Lee$^c$ Y. Setiawan$^c$ and K. M. Hoe$^d$

$^a$School of Electrical and Electronic Engineering, and $^b$School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798
$^c$Institute of Materials Research Engineering, Singapore 117602
$^d$Institute of Microelectronics, Singapore 117685

We studied erbium germanosilicide films formed on relaxed p-type $\text{Si}_{1-x} \text{Ge}_x (100) \ (x = 0–0.3)$ virtual substrates by conventional rapid thermal annealing (RTA) at temperatures of 500–700°C. Two dimensional X-ray diffraction and pole figure measurements revealed that the silicide films formed were epitaxial $\text{Er} (\text{Si}_{1-x} \text{Ge}_x)_{2-y}$ with orientation relationship $\text{Er} (\text{Si}_{1-x} \text{Ge}_x)_{2-y}, [\overline{1}000] \parallel \text{Si}_{1-y} \text{Ge}_y (001) \parallel [100]$ or $\text{Er} (\text{Si}_{1-x} \text{Ge}_x)_{2-y}, [1100] \parallel \text{Si}_{1-y} \text{Ge}_y (001) \parallel [110]$. Schottky barrier height, $\Phi_{\text{B}}$, of the $\text{Er} (\text{Si}_{1-x} \text{Ge}_x)_{2-y}/p – \text{Si}_{1-y} \text{Ge}_y (100)$ contact was found to decrease from 0.79 to 0.62 eV with increasing Ge (from 0 to 30%), implying a slight increase in its barrier height for electrons, $\Phi_{\text{B}}$, from 0.33 to 0.37 eV.

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Silicon germanium is being used in high-speed complementary metal oxide semiconductors (CMOSs) in the source/drain region for mobility enhancement by inducing channel strain, and in $\text{Si}/\text{SiGe}/\text{Si}$ heterostructure bipolar transistors (HBTs) for gigahertz bandwidth communications. For these applications, it is advantageous to incorporate metal silicide thin films so as to increase device drive current and to enhance the speed of an electronic circuit. Ni germanosilicides have several advantages, including low formation temperature, low Schottky barrier height, $\Phi_{\text{B}}$, on n-type silicon compared to other metal silicide/n-Si systems (−0.3 eV vs −0.65 eV for $\text{ErSi}_2$ and NiSi, respectively). In addition, they can be epitaxially grown on Si(001) with a high crystallographic quality, which results in greater morphological stability and homogeneous Schottky barriers.

The formation of erbium silicide on Si has been reported to result in microstructural defects, such as pits, pinholes, and pyramids, which result in degraded silicide/silicon interfaces, which may cause increasing leakage currents. However, research on the solid phase reaction between erbium and silicon germanium have been limited. Travlos et al. have reported the material properties of epitaxial erbium silicide formed on Ge-implanted silicon as well as strained and relaxed $\text{Si}_{1-x} \text{Ge}_x$ in this paper, we report the formation of epitaxial Er-germanosilicide films fabricated by rapid thermal annealing (RTA) of thin Er films on lightly doped p-$\text{Si}_{1-x} \text{Ge}_x (001)$ ($x = 0–0.3$) substrates at temperatures of 500–700°C. Materials characterization was conducted using two-dimensional (2D) X-ray diffraction (XRD), cross-sectional transmission electron microscopy (XTEM), and secondary ion mass spectrometry (SIMS). Electrical measurements were performed on Er germanosilicide Schottky diodes to elucidate the junction characteristics of erbium germanosilicide/$\text{Si}_{1-x} \text{Ge}_x$ interface.

Experimental

p-Doped relaxed $\text{Si}_{1-x} \text{Ge}_x$ virtual wafers [1 $\mu$m relaxed $\text{Si}_{1-x} \text{Ge}_x$ layers were grown on 2 $\mu$m thick $\text{Si}_{1-y} \text{Ge}_y$, graded layer on Si(001)] with a Ge atomic percentage of 0–30% were used as starting substrates. The wafers were cleaned using 1:4 $\text{H}_2\text{O}_2$:H$_2$SO$_4$ for 3 min, then dipped in dilute HF for 1 min prior to the deposition of a 50 nm thick erbium film at room temperature in a dc magnetron-sputtering chamber with a base pressure of $3 \times 10^{-7}$ Torr. In some samples, a contact mask with 1 mm diameter circular holes was used as a physical barrier for selective erbium deposition during the sputter deposition process. The Er deposition was followed by a sequential deposition without breaking vacuum of 50 Å Ti and 200 Å TiN double capping layer, which serves to minimize oxidation. RTA was then carried out with an XMS8 rapid thermal annealing system using an optimized condition of 500–700°C in a N$_2$ ambient for 60 s. A 2000 Å Au was deposited on the back side of the wafers with circular Er-silicide dots to form ohmic contact for electrical measurements.

Results and Discussion

The phases of the Er-silicide films formed were identified using X-ray diffraction [Bruker D8 general area detector diffraction system (GADDS) equipped with a two-dimensional detector]. Figure 1 shows typical two-dimensional (2D) XRD patterns obtained...
for Er films deposited on Si$_{0.8}$Ge$_{0.2}$(001) after RTA at 600°C for 60 s. [Similar 2D XRD patterns were obtained for Er films on Si(001), Si$_{0.8}$Ge$_{0.2}$(001), and Si$_{0.9}$Ge$_{0.1}$(001)]. Each pattern, i.e., Debye diffraction ring, is a plot of diffraction intensity for a particular diffraction angle 2θ (x-axis) with χ (y-axis). High intensity and well-defined spots, either located in the center of the Debye diffraction ring (i.e., χ = 0°) or off-center positions, symmetrically, are due to diffractions from highly textured or even epitaxial film, whereas polycrystalline film would be typified by rings with uniformly distributed intensity.

Figure 1 shows the (1100), (2200), and (1101) peaks of AlB$_2$ hexagonal erbium disilicide, indicating that the germanosilicide phase is Er(Si$_{1-x}$Ge$_x$)$_{2−y}$ (x = 0.2). The observation of the 2D XRD patterns identical to that from Er film on Si(001) substrate, coupled with pole figure analysis of the same figure (see Fig. 2), further indicates that the Er(Si$_{1-x}$Ge$_x$)$_{2−y}$ films are also epitaxial, as in the case of ErSi$_2$ films formed on Si(001) [10] with orientation relationships Er(Si$_{1-x}$Ge$_x$)$_{2−y}$[1100][0001] || Si$_{1-x}$Ge$_x$(001)[110]. The fourfold symmetry of the (1100) poles, rather than the twofold symmetry expected if the Er(Si$_{1-x}$Ge$_x$)$_{2−y}$ were a single crystal, confirms that the Er(Si$_{1-x}$Ge$_x$)$_{2−y}$ film contains both regions where the [0001] (i.e., c-axis) is parallel to Si [110] and where it is parallel to Si [110] (i.e., also containing grains with orientation relationship Er(Si$_{1-x}$Ge$_x$)$_{2−y}$[1100][0001] || Si$_{1-x}$Ge$_x$(001)[110], in agreement with the previous reports on epitaxial erbium disilicide on Si(001). The d-spacing of the (1100) planes for Er(Si$_{1-x}$Ge$_x$)$_{2−y}$ (x = 0–0.3) (extracted from the experimental 20 values) are 0.48–0.87% larger than the corresponding values for the relaxed Er(Si$_{1-x}$Ge$_x$)$_{2−y}$ (x = 0–0.3) film. The relaxed Er(Si$_{1-x}$Ge$_x$)$_{2−y}$[1100] d-spacing was found by using Vegard’s law for an ideal solid solution [14] i.e., treating Er(Si$_{1-x}$Ge$_x$)$_{2−y}$ as a solid solution of ErSi$_2$ and ErGe$_2$ on the calculated d-spacing of ErSi$_{1.67}$ and ErGe$_{1.5}$. The observation of larger d-spacing of the (1100) planes from the θ − 2θ XRD measurement is certainly due to the presence of a biaxial and compressive strain in the epitaxial Er(Si$_{1-x}$Ge$_x$)$_{2−y}$ film [−2.7% for ErSi$_2$–x] [Ref. 10], which results in the increase of the d-spacing of the Er(Si$_{1-x}$Ge$_x$)$_{2−y}$[1100] planes oriented parallel to the (001) Si substrate plane. Also observed in Fig. 2 are weak peaks of the orientation Er(Si$_{1-x}$Ge$_x$)$_{2−y}$[1012] ×[0110] || Si$_{1-x}$Ge$_x$(001)[010], which have also been observed for Er-germanide.

Despite the use of the TiN/Ti capping layer, small traces of Er$_2$O$_3$ and Er$_2$SiO$_4$Er(SiGeO)$_3$ are detected due to the oxidation of the extremely reactive Er in the annealing ambient. However, it must be said that the samples showed a stronger Er(Si$_{1-x}$Ge$_x$)$_{2−y}$ (1100) peak and greatly reduced Er$_2$O$_3$ and Er$_2$SiO$_4$Er(SiGeO)$_3$ peaks compared to the samples without the TiN/Ti capping. In addition, it has been previously reported that Ti capped Er/Si$_{1-x}$Ge$_x$ (x = 0.088) samples have also shown suppression of Er$_2$SiO$_5$ XRD peaks and improvement in phase formation [15].

Figure 3 shows the XRD 2θ plots of Er(Si$_{1-x}$Ge$_x$)$_{2−y}$ samples with Ge concentrations x = 0–0.3. The XRD plots show that there is a left shift of the Er(Si$_{1-x}$Ge$_x$)$_{2−y}$[1100] (1100) peak position, which corresponds to an increasing spacing of the Er(Si$_{1-x}$Ge$_x$)$_{2−y}$[1100] lattice planes, with increasing Ge concentration in SiGe substrate. The increase of lattice constants in Er(Si$_{1-x}$Ge$_x$)$_{2−y}$ is certainly due to the fact that AlB$_2$ hexagonal erbium digermanide Er$_2$Ge$_2$ has larger lattice constant a = b = 3.889 Å as compared to the corresponding value of a = b = 3.798 Å for AlB$_2$ hexagonal erbium disilicide ErSi$_{2−y}$, in accordance with Vegard’s law for ideal solid solution.

Figure 4 shows a XTEM micrograph of the Er-germanosilicided Si$_{1-x}$Ge$_x$ (x = 0.2) films annealed at 600°C. From the results (see Fig. 4a, top micrograph taken at a lower magnification), it is observed that the Er-germanosilicided film is uniform with a thickness of ~85 nm (with 16 nm TiN capping). The Er-germanosilicide/ Si$_{0.8}$Ge$_{0.2}$ interface is smooth with no evidence of agglomeration or Ge segregation, which is typically observed for Ni germanosilicide films annealed at >500°C [16]. The high-resolution TEM micrograph of the same sample (Fig. 4b, bottom micrograph) shows that the Er-germanosilicided film is indeed epitaxial to the underlying Si$_{0.8}$Ge$_{0.2}$ substrate: almost a 1:1 relationship is observed for the Er(Si$_{1-x}$Ge$_x$)$_{2−y}$[1101] and Si(111) lattice planes across the interface as expected for Er(Si$_{1-x}$Ge$_x$)$_{2−y}$[1100][0001] || Si$_{1-x}$Ge$_x$(001)[110] orientation relationship. The TEM/energy dispersive X-ray (EDX) compositional analysis shows that the ratio of Si/Ge at the substrate regions labeled 1 is around 81.3:18.7 (±5%) while the ratio of Er:Si:Ge at the Er-germanosilicided regions labeled 2 is around 31.4:56.4:12.3 (±6%). It is noted that the Si/Ge ratio (~4.58 in the Er(Si$_{1-x}$Ge$_x$)$_{2−y}$ layer is essentially equal to that in the underlying SiGe substrate, i.e., ~4.35, indicating that the Si/Ge ratio is maintained in the silicide layer after the reaction of Er with the Si$_{0.8}$Ge$_{0.2}$ substrate.

Figure 5 shows the secondary ion mass spectroscopy (SIMS) depth profiles of the Er-germanosilicided samples with Ge concentrations (x = 0.1–0.3). Figure 5 shows that layered structures of
Er(\text{Si}_{1-x}\text{Ge}_x)_{2-y}$ of similar thicknesses were formed in all three samples, which correspond to the relative flat portions of the erbia, silicon, and germanium signals. To investigate the uniformity of the Er(\text{Si}_{1-x}\text{Ge}_x)_{2-y} layers, we calculated the ratio of Si to Er and found that the Si count is constant from the Er(\text{Si}_{1-x}\text{Ge}_x)_{2-y}/Si interface toward the surface until ~50 nm from the surface, whereby the Si counts decreases by 0.52%/nm. This decrease occurs until ~25 nm from the surface, whereby the interference of the oxygen and titanium signals interferes with the calculation. The decreasing Si count from 50 nm onward toward the surface can be understood on the basis that Si/Ge is the diffusing species in the Er to Si$_{1-x}$Ge$_x$ solid-state reaction. For a RTA time of 60 s, the Er(\text{Si}_{1-x}\text{Ge}_x)_{2-y} film is unable to achieve its preferred stoichiometry \([\text{Er}(\text{Si}_{1-x}\text{Ge}_x)_{2-y}]_{1.67}\).

\[
\Delta \Phi = \sqrt{\frac{qE}{4\pi\varepsilon_i}}
\]  

with \(E = \left(\frac{2qN_a/N_v}{\varepsilon_i} [V_{th} - V - (kT/q)]\right)^{1/2}\) as the maximum electric field, \(\varepsilon_i\) is the permittivity determined from Ref. 14, \(V_{th}\) is the built-in potential, and \(N_a\) is the acceptor concentration both determined by capacitance-voltage measurements. By assuming the bandgap \(E_g = q\phi_{Bp} + \phi_{Bn}\) and using the relationship, \(E_g = 1.12 - 0.41x + 0.008x^2\) eV,\(^{14}\) between \(E_g\) and Ge content \(x\) in Si$_{1-x}$Ge$_x$, the barrier height for electron injection, i.e., \(\phi_{Bp}\), were also calculated.

It is known that in Si$_{1-x}$Ge$_x$, the reduction of bandgap \(E_g\) with increasing Ge content \(x\) is purely due to the change (i.e., moving up) of valence band edge \(E_v\) position as the conduction band edge position, \(E_c\), changes only slightly with respect to \(x\) (note: \(E_c\) position relative to vacuum level is related to \(x\) by \(E_c = -4.05 + 0.05x\)).\(^{20}\) It was also found that the workfunction of Er-germanide is ~0.3 eV larger than that of Er-silicide,\(^{21}\) suggesting a deeper Fermi-level position (relative to vacuum level) for Er(\text{Si}_{1-x}\text{Ge}_x)_{2-y} as compared to ErSi$_2$\(^{2}\). That provided that the workfunction of Er(\text{Si}_{1-x}\text{Ge}_x)_{2-y} varies monotonically with \(x\). As the barrier height for hole \(\phi_{Bn}\) is more or less the difference between metal Fermi level \(E_{\text{fin}}\) and \(E_c\), it is appropriate to assume that the reduction in \(\phi_{Bp}\) with increasing \(x\) is hence, the Si deficiency nearer to the surface. The results in Fig. 5 also show that oxygen penetration was effectively suppressed and mostly confined at the TiN/Ti capping layer, illustrating that the TiN/Ti capping layer is effective in blocking oxygen diffusion during RTA.

The \(I-V\) characteristics of the formed Er-germanosilicided diodes \((x = 0.1–0.3)\) as well as the control diode [i.e., ErSi$_2$/(p-Si(001))] were measured, as shown in Fig. 6. As shown, both reverse current and forward saturation current increase with increasing Ge content in the substrate. Because typical ideality factors obtained from these diodes are 1.05–1.15, which is much smaller than 2 but close to 1, the increase in the reverse current and forward saturation current must be due to the reduction in the Schottky barrier height \(\phi_{Bp}\) due to the increasing Ge content.

In order to experimentally determine \(\phi_{Bp}\), temperature-dependent \(I-V\) curves were measured on these diodes. The associated saturation current \(I_{sat}\) values were obtained by extrapolating the log\(|I| - \exp(-eV/kT)|\) vs. \(V\) curve to \(V = 0\) (see Fig. 7a as an example). From the slopes of Richardson plots (shown in Fig. 7b), i.e., the plot of \(\log(I_{sat}/T^2)\) against \(1/T\), the effective barrier height \(\phi_{Bp}\) values were calculated. Figure 8 shows the actual barrier height \(\phi_{Bp}\) values after taking into account image-force–induced barrier lowering \(\Delta \Phi\) by using the well-known relation:\(^{19}\)

\[
\Delta \Phi = \sqrt{\frac{qE}{4\pi\varepsilon_i}}
\]  

\(E = \left(\frac{2qN_a/N_v}{\varepsilon_i} [V_{th} - V - (kT/q)]\right)^{1/2}\) as the maximum electric field, \(\varepsilon_i\) is the permittivity determined from Ref. 14, \(V_{th}\) is the built-in potential, and \(N_a\) is the acceptor concentration both determined by capacitance-voltage measurements. By assuming the bandgap \(E_g = q\phi_{Bp} + \phi_{Bn}\) and using the relationship, \(E_g = 1.12 - 0.41x + 0.008x^2\) eV,\(^{14}\) between \(E_g\) and Ge content \(x\) in Si$_{1-x}$Ge$_x$, the barrier height for electron injection, i.e., \(\phi_{Bp}\), were also calculated.

It is known that in Si$_{1-x}$Ge$_x$, the reduction of bandgap \(E_g\) with increasing Ge content \(x\) is purely due to the change (i.e., moving up) of valence band edge \(E_v\) position as the conduction band edge position, \(E_c\), changes only slightly with respect to \(x\) (note: \(E_c\) position relative to vacuum level is related to \(x\) by \(E_c = -4.05 + 0.05x\)).\(^{20}\) It was also found that the workfunction of Er-germanide is ~0.3 eV larger than that of Er-silicide,\(^{21}\) suggesting a deeper Fermi-level position (relative to vacuum level) for Er(\text{Si}_{1-x}\text{Ge}_x)_{2-y} as compared to ErSi$_2$\(^{2}\). That provided that the workfunction of Er(\text{Si}_{1-x}\text{Ge}_x)_{2-y} varies monotonically with \(x\). As the barrier height for hole \(\phi_{Bn}\) is more or less the difference between metal Fermi level \(E_{\text{fin}}\) and \(E_c\), it is appropriate to assume that the reduction in \(\phi_{Bp}\) with increasing \(x\) is...
mainly due to the change (i.e., moving up) of \( E_c \) position, and, to a certain extent, the change (i.e., moving down) of \( E_{\text{in}} \) position. The slight increase in \( \phi_{\text{bim}} \) with \( x \) is largely due to the change in \( E_{\text{in}} \) position with additional contribution by the change (i.e., moving up) in \( E_c \) position (note: \( \Delta E_c \) is only 15 meV for \( x = 0.3 \) while \( \Delta \phi_{\text{bim}} \approx 52 \) meV). The electron barrier height of NiSi\(_{1-x}\)Ge\(_x\) (\( x = 0, 0.3 \)) is also plotted in Fig. 8 and, as can be seen, is larger than the electron barrier height of ErSi\(_{1-x}\)Ge\(_x\) by \(-0.3 \) eV. The larger barrier height results in a larger contact resistance \( R_{\text{on}} \) for NiSi(NiSi\(_{1-x}\)Ge\(_x\))/n-SiSiGe systems (e.g., source-drain contact of N-MOS transistors, etc.). Note that a 0.3 eV larger barrier height would result in a larger \( R_{\text{on}} \) by \(-1 \) order of magnitude considering a semiconductor doping concentration of \( \sim 10^{20} \) cm\(^{-3}\).  

Figure 8. Schottky barrier height to holes, \( \phi_{\text{bim}} \), and electrons, \( \phi_{\text{bim}} \), of the Er(Si\(_{1-x}\)Ge\(_x\))\(_2-y/p\)-Si\(_{1-x}\)Ge\(_x\) diodes (\( x = 0-0.3 \)) and Schottky barrier height to electrons of NiSi\(_{1-x}\)Ge\(_x)/n\)-Si\(_{1-x}\)Ge\(_x\) diodes (\( x = 0.03 \)) from Ref. 22. Varying bandgap, \( E_g \), with Ge concentration is also plotted. \( \phi_{\text{bim}} \) calculated using the relation \( E_g = q(\phi_{\text{bim}} + \phi_{\text{bim}}) \).

Figure 7. (a) Temperature dependent \( \log(I/(1 - \exp(-eV/kT))) \) \( I-V \) plots measured on Er(Si\(_{1-x}\)Ge\(_x\))\(_2-y\) diodes \( x = 0.2 \) with typically low leakage currents. (b) Richardson’s plot for Er(Si\(_{1-x}\)Ge\(_x\))\(_2-y\) diodes \( x = 0-0.3 \).

Conclusion

We have fabricated epitaxial growth of erbium germanosilicide on relaxed Si\(_{1-x}\)Ge\(_x\) (\( x = 0-0.3 \)) substrates with orientation relationship Er(Si\(_{1-x}\)Ge\(_x\))\(_2-y\)(1\(\bar{1}\)00)[0001] \( \parallel \) Si\(_{1-x}\)Ge\(_x\)(001)[110] or Er(Si\(_{1-x}\)Ge\(_x\))\(_2-y\)(1\(\bar{1}\)00)[0001] \( \parallel \) Si\(_{1-x}\)Ge\(_x\)(001)[110]. Electrical characteristics indicate that the Er-germanosilicide/Si\(_{1-x}\)Ge\(_x\) interfaces are near ideal with decreasing Schottky barrier height, \( \phi_{\text{bim}} \), from 0.79 to 0.62 eV of Er-germanosilicide (from 0–30%). This implies a slight increase in its barrier height for electrons, \( \phi_{\text{bim}} \), from 0.33 to 0.37 eV. Thus Er-germanosilicide can potentially be used as a high-quality contact to Si\(_{1-x}\)Ge\(_x\) for advanced nanodevice applications, including Si-based optoelectronic devices, Si/SiGe HBTs, and CMOS applications.

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