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Phase stabilities of ternary rare earth metal disilicides

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ABSTRACT Chen et al. recently carried out self-assembled growth of epitaxial sub-10 nm erbium disilicide ($C32$, $hP3$) nanowires on Si(001). They pointed out that the success of this self-assembly process is due to asymmetric lattice mismatches in the two orthogonal crystallographic directions of the two materials, i.e. $[0001]_{ErSi_2}/[1\bar{1}0]_{Si}$,+6.5% and $[11\bar{2}0]_{RESi_2}/[110]_{Si}$,−1.3%. In this paper, we have established experimentally that $(Er_{1-x}Gd_x)Si_2$ and $(Er_{1-x}Sm_x)Si_2$ exist with values of x from 0 to 1 and that their lattice parameters follow Vegard's law. Since the binary $GdSi_2$ and $SmSi_2$ end members in each of these ternary systems have a and c unit cell parameters greater than those of the $ErSi_2$ end member, we have determined that an optimal lattice mismatch can be achieved with the Si substrate at a composition of $(Er_{0.45}Gd_{0.55})Si_2$ and $(Er_{0.62}Sm_{0.38})Si_2$. It is reasonable to expect a higher quality of self-assembled nanowire growth on Si by employing these ternary silicides. A review of the atomic sizes of the rare earth metal elements of the lanthanide series indicates that many of the binary disilicides, when exhibiting the $C32$ structure, should have a tendency to form ternary and higher-order disilicides. These materials would offer many possibilities for the growth of silicide nanowires with interesting electronic, magnetic and optical properties.

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1 Introduction

Recent results, including those of Chen et al. [1], in growing self-assembled erbium (as well as other rare earth metal) disilicide ($ErSi_2$) nanowires on silicon have opened up a new avenue for the fabrication of one-dimensional nanoscale features for potential applications in molecular electronics [1–6]. These nanowires were grown by taking advantage of the asymmetric lattice mismatch of two crystallographic directions in the hexagonal erbium disilicide ($C32$, $hP3$, AlB_2 structure) with respect to the two perpendicular Si⟨110⟩ directions on Si(001). As shown in Fig. 1, when $ErSi_2$ is bonded to Si, the Si atoms in the disilicide, marked as A, B, C and D, could replace those on the Si(001) surface that are marked as A′, B′ C′ and D′. (For the purpose of clarity, only Si atoms on the (001) planes are shown.) This bonding geometry maintains the bulk-like Si–Si bonds in each respective crystal lattice on either side of the interface. However, while the lattice mismatch between A–B (D–C) and A′–B′ (D′–C′) (see Fig. 1) is only −1.3%, that between A–D (B–C) and A′–D′ (B′–C′) is +6.5%, based on the known lattice parameters of $ErSi_2$ and Si [7]. It is worth noting that we have adopted the convention in the present communication that positive (negative) lattice mismatches indicate that the lattice parameters of the silicide are larger (smaller) than those of silicon. The arrangement of Si atoms in this figure is greatly exaggerated to show the asymmetric mismatches in the two crystallographic directions along the $[11\bar{2}0]_{ErSi_2}/[110]_{Si}$ and $[0001]_{ErSi_2}/[1\bar{1}0]_{Si}$ directions.

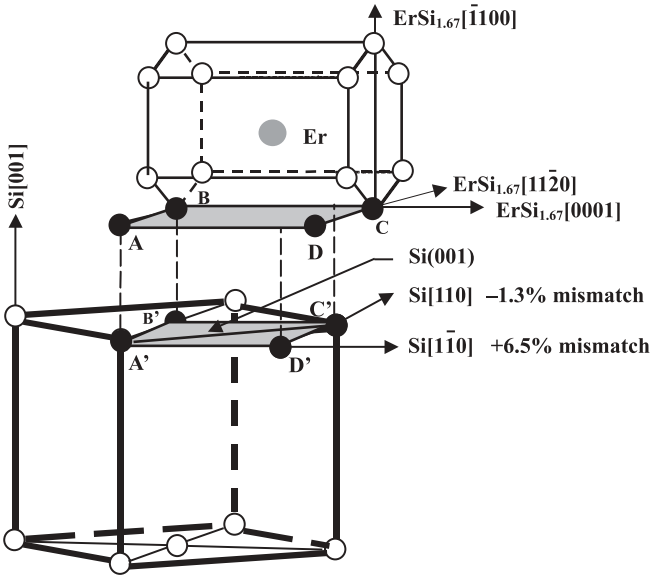

FIGURE 1 The crystallographic relationships between $ErSi_2$ and Si. For clarity only Si atoms on the (001) planes are shown. One Er atom is shown as a gray solid circle. The four Si atoms of $ErSi_2$, shown as solid circles, are denoted as A, B, C, and D, while those of Si are shown as A′, B′, C′ and D′, respectively

This asymmetric lattice mismatch in the two orthogonal directions enables one to grow sub-10-nm nanowires [1–6]. A review of the lattice parameters of a number of rare earth

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metal disilicides [7] ($RESi_2$) shows that the lattice mismatches in the $[0001]_{RESi_2}/[1\bar{1}0]_{Si}$ directions are all large and positive while those in the $[11\bar{2}0]_{RESi_2}/[110]_{Si}$ directions are small but can be either positive or negative. A carefully chosen composition of a ternary rare earth disilicide that consists of binary end members with opposite-signed mismatches with the Si⟨1$\bar{1}$0⟩ directions would have a perfect lattice match in the $[11\bar{2}0]_{RESi_2}/[110]_{Si}$ directions while maintaining a rather large mismatch in the other direction. It seems reasonable to conclude that one may be able to grow better quality disilicide nanowires using such a ternary rare earth metal disilicide. A ternary disilicide $(RE_{1-x}RE'_x)Si_2$ can also be thought of as an alloy or solid solution of the two rare earth metal disilicides $RESi_2$ and $RE'Si_2$, where RE and RE′ are different rare earth elements. In view of the small difference in the atom sizes for many of the rare earth metals, one could expect that continuous solid solutions for many of the ternary rare earth metal disilicides exist at high temperatures. We report in this communication that, indeed, two such solid solutions, i.e. $(Er_{1-x}Gd_x)Si_2$ and $(Er_{1-x}Sm_x)Si_2$, do exist. The phase stabilities of these two ternary disilicides are determined experimentally by examining the lattice parameters of ternary disilicides using metallurgical techniques.

2 Experimental

Samples of binary $ErSi_2$, $GdSi_2$ and $SmSi_2$, as well as the two ternary disilicides $(Er_{1-x}Gd_x)Si_2$ and $(Er_{1-x}Sm_x)Si_2$, were prepared first by arc melting appropriate ratios of high-purity starting materials. The three rare earth metals used had a purity of 99.9% (metal basis) while the Si material that was used had a purity of 99.9999%. Despite the fact that these materials are referred to as 'disilicides' and that the nomenclature that we use for these phases is $RESi_2$, the actual chemical composition is closer to $RESi_{1.67}$ [8]. The arc-melted ingots of these silicides were turned over more than three times in vacuum and remelted to achieve proper intermixing of the elements. They were then wrapped with tantalum foil, sealed in a quartz capsule filled with ultrahigh-purity (UHP) argon of 99.998%, and annealed at 1000 °C for ten days prior to an ice-water quench. It is important to note that some of the ternary disilicide samples were prepared using appropriate amounts of prepared binary disilicides as the starting materials. Powders of the annealed samples were obtained by pulverizing the arc-melted ingots with a mortar and pestle. To relieve accumulated mechanical stress from the pulverization process, the powders were annealed in an evacuated quartz tube filled with UHP argon at 600 °C and quenched in ice-water mixtures. X-ray diffraction was performed with a Phillips X-ray diffractometer with Cu K_α radiation. Scans were typically taken over a 2θ range of 20 to 90°. Silicon powder was used as an internal standard.

3 Results and discussion

X-ray diffraction patterns of the two ternary disilicides, $(Er_{1-x}Gd_x)Si_2$ and $(Er_{1-x}Sm_x)Si_2$, are presented in Fig. 2. Peaks from the Si internal standard can be seen in the patterns. The crystal structures of both silicides were determined to be the AlB_2 structure, as expected. The peaks of the pattern can be seen to shift to the left as the Gd or Sm content

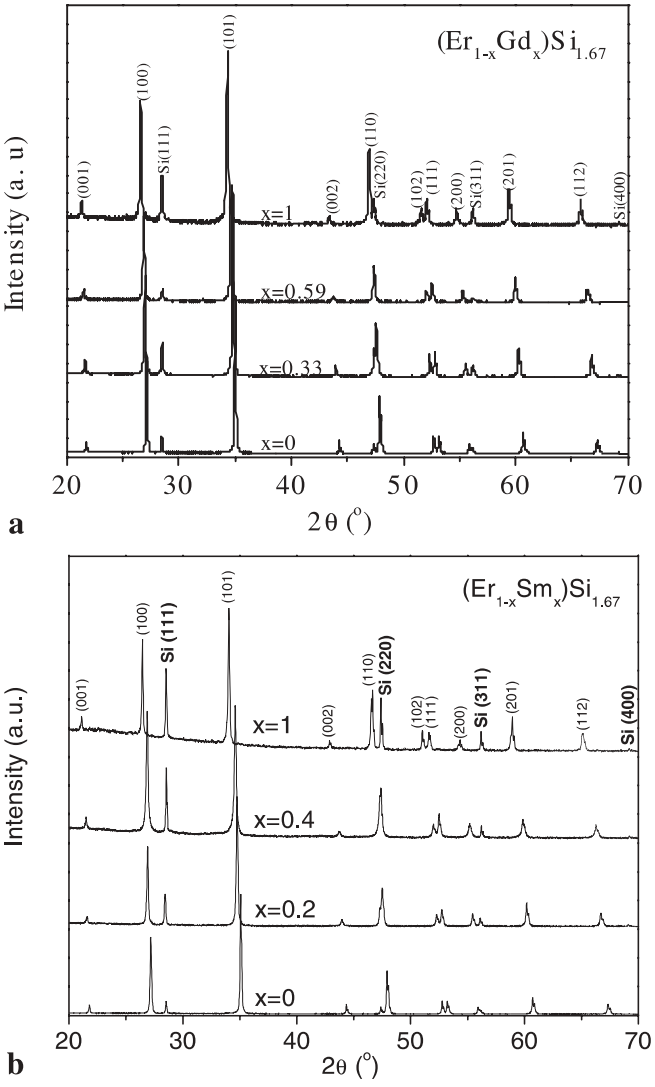

FIGURE 2 X-ray diffraction patterns of two ternary disilicides, $(Er_{1-x}Gd_x)Si_2$ and $(Er_{1-x}Sm_x)Si_2$ at room temperature, where x is the mole fraction of either Gd or Sm

is increased, signifying an increase in the lattice parameters as the comparatively larger Gd or Sm atoms are incorporated into the lattice. Using the Si standard, the lattice parameters of these two ternary disilicides were determined as shown in Fig. 3 and Table 1 [9–12]. The lattice parameters were obtained by extrapolation using both the Nelson and Riley and Cohen methods [13–15]. The differences in the lattice parameters obtained for a specific sample using the two methods are within ±0.00001 nm. However, when we compare the experimental results obtained from different samples of the same silicide, the variations are larger. We thus estimate the uncertainties in these parameters to be ±0.0001 nm.

Within the uncertainties of the measured values, the a and c lattice parameters, as well as the c/a ratios (not plotted), vary linearly with composition in accordance with Vegard's law. Thus, there is no question that $ErSi_2$ forms continuous solutions with either $GdSi_2$ or $SmSi_2$. The measured lattice parameters of these disilicides, and the known value of Si at room temperature, show that the lattice mismatch in the $[0001]_{RESi_2}/[1\bar{1}0]_{Si}$ directions varies from +6.5% when

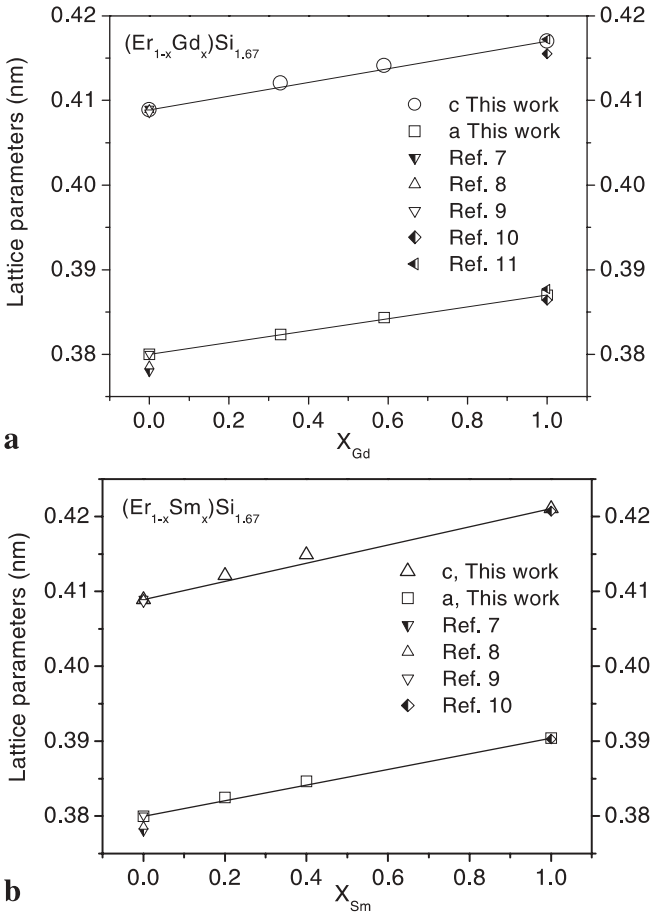

FIGURE 3 Room temperature lattice parameters of the two ternary silicides, $(Er_{1-x}Gd_x)Si_2$ (**a**) and $(Er_{1-x}Sm_x)Si_2$ (**b**)

	a	*c*	Ref.
$ErSi_{1.67}$	0.378	0.409	7
	0.3786	0.4089	8
	0.38006	0.40856	9
	0.37980 ± 0.0001	0.40880 ± 0.0001	This work
$GdSi_{1.67}$	0.3864	0.4155	10
	0.3877	0.4172	11
	0.38725 ± 0.0001	0.41720 ± 0.0001	This work
$SmSi_{1.67}$	0.3903	0.4207	10
	0.39040 ± 0.0001	0.42105 ± 0.0001	This work

TABLE 1 Lattice parameters of the binary rare earth silicides (nm)

$x = 0$ (pure $ErSi_2$) to $+8.6\%$ when $x_{Gd} = 1$ (pure $GdSi_2$) or $+9.6\%$ when $x_{Sm} = 1$ (pure $SmSi_2$). In contrast, the lattice mismatch in the $[11\bar{2}0]_{RESi_2}/[110]_{Si}$ directions varies from -1.3% (pure $ErSi_2$) to $+0.8\%$ (pure $GdSi_2$) or $+1.67\%$ (pure $SmSi_2$). According to these data, either $(Er_{0.62}Sm_{0.38})Si_2$ or $(Er_{0.45}Gd_{0.55})Si_2$ would have near perfect lattice match in the $[11\bar{2}0]_{RESi_2}/[110]_{Si}$ directions, as can be seen by the near coincidences of the (110) diffraction peaks of $(Er_{0.60}Sm_{0.40})Si_2$ and $(Er_{0.41}Gd_{0.59})Si_2$ with the Si(220) peak shown in Fig. 2. However, each would retain sufficient lattice mismatches in the $[0001]_{RESi_2}/[1\bar{1}0]_{Si}$ directions necessary for the self-assembled growth of the nanowire structure. Therefore, both of these ternary rare earth disilicides are worthy choices for growing nanowires of improved quality over those already achieved using binary rare earth disilicide materials [1–6]. A review of the atomic sizes of the rare earth elements from the lanthanide series [16] indicates that many of the binary disilicides, when exhibiting the AlB_2 structure, would have the tendency to form ternary and higher order disilicides. This offers many new possible materials for growing silicide nanowires.

4 Conclusion

In summary, we have experimentally determined that solid solutions of $(Er_{1-x}Gd_x)Si_2$ and $(Er_{1-x}Sm_x)Si_2$ exist over the entire composition range between the respective binary end members and that the *a* and *c* unit cell parameters vary linearly with the mole fraction of $ErSi_2$, in agreement with Vegard's law. While the lattice mismatches in the $[0001]_{RESi_2}/[1\bar{1}0]_{Si}$ directions are both positive and large, those in the $[11\bar{2}0]_{RESi_2}/[110]_{Si}$ directions are small and vary from negative for pure $ErSi_2$ to positive for either $GdSi_2$ or $SmSi_2$. Accordingly, $(Er_{0.45}Gd_{0.55})Si_2$ and $(Er_{0.62}Sm_{0.38})Si_2$ would have a perfect lattice match in the Si⟨110⟩ growth direction, which is likely to lead to better quality nanowires that can grow with higher length-to-width aspect ratios and have the ability to withstand higher annealing temperatures without forming defects.

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