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Vacancy concentrations in binary rare-earth disilicides with the aluminum diboride structure

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ABSTRACT Recent success in growing sub-10-nm rare-earth disilicide nanowires on Si(001) by Chen et al. has stimulated great interest in understanding the point defects in these silicides that may affect their properties. These disilicides exhibiting the AlB_2 structure (C32, hP3) have the formula of $RESi_{1.67}$, suggesting the existence of vacancies on the Si sublattice sites. In the present study, we obtain the vacancy concentrations by simultaneously measuring their lattice parameters and bulk densities. The results show 11.1% vacancies expressed in terms of one mole of $RESi_2$. This means that in a unit cell of nine sites, one of the six sites occupied by the Si atoms is vacant.

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1 Introduction

As a part of our on-going research on the phase stabilities of rare-earth-metal disilicides and the growth of these disilicide nanowires [1–4] on a substrate of silicon, we carried out a systematic investigation of the point defects in rare-earth-metal disilicides. The existence of these point defects may affect the quality and the properties of these silicide nanowires. In the present study, we report the results obtained on the point defects and their concentrations in binary disilicides of Dy, Er, Ho and Y that exhibit the AlB_2 structure (C32, hP3). Even though they all exhibit the AlB_2 structure, these disilicides have been reported to have the approximate formula $RESi_{1.67}$ [5–9], with RE denoting the rare-earth metals. These results suggest that vacancies exist on the silicon sublattice, consistent with the rather large size differences between Si and the RE metals [10]. In other words, with deviations from the ideal composition, RE atoms normally occupying their own sublattice sites cannot substitute for Si atoms, resulting in the formation of vacancies on the Si sublattice. Indeed, a transmission electron microscopy study of an epitaxial YSi_{2-x} thin film on Si(111) by Lee et al. [11] suggested that one of the six Si atoms on the Si sublattice is vacant. In the present study, we determine the vacancy concentrations in these silicides using the Simmons–Balluffi technique [12, 13]. This technique, consisting of simultaneously measuring the lattice parameters and bulk densities, has been used extensively in obtaining the vacancies in pure metals and intermetallic compounds [12–17].

2 Experimental

Samples of these disilicides were prepared by arc melting high-purity elements (99.999% Si and 99.9% metals) in the appropriate ratio of 1 mole metal to 1.67 moles Si. Arc melting was carried out in an atmosphere of Ti-deoxidized ultra-high-purity (UHP) argon of 99.998% at a pressure of 40 mTorr. The arc-melted disilicide in-

gots were turned over three times in order to promote intermixing. Weight loss during the course of arc melting was found to be less than 1% with the sample weight being about 0.5 g. Each of the ingots was subsequently wrapped with a tantalum foil, contained in a quartz capsule, evacuated to a pressure of 7.5×10^{-7} Torr, filled with Ti-deoxidized UHP argon, annealed at 1000 °C for 10 days, and then quenched in an ice–water bath. X-ray diffraction was carried out using a STOE X-ray diffractometer with Cu K_α radiation. Scans were typically taken over a 2θ range of 20° to 90° at the 0.02° step size with silicon used as an internal standard. Bulk densities were measured using an AccuPyc 1330 pycnometer made by Micromeritics Corporation. In using this technique, the powder samples were first degreased and then weighed in air ambient. Each of the density measurements was repeated 99 times and the reproducibility of volume values was found to be better than 0.0005 cm³.

3 Data analysis and discussion

Prior to presenting the vacancy concentrations obtained for these disilicides from the X-ray and bulk densities, we would like to present a brief derivation of the equation to calculate the vacancy concentrations. The expression for the X-ray density, ϱ_x, given below is obtained assuming that all the α-sublattice sites are occupied by the A atoms and all the β-sublattice sites by the B atoms,

$$\varrho_x = \frac{\left(N_s^\alpha M_A + N_s^\beta M_B\right)/N_0}{V \times (N_s/n)}, \quad (1)$$

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where N_s^α is the number of the α-sublattice sites occupied by the A atoms and N_s^β that of the β-sublattice sites occupied by the B atoms, the total number of lattice sites is $N_s = N_s^\alpha + N_s^\beta = (N_A^\alpha + N_v^\alpha) + (N_B^\beta + N_v^\beta)$, M_A and M_B are the atomic weights of A and B, N_v^α and N_v^β are the number of vacancies on the α-sublattice and the β-sublattice, respectively, N_0 is the Avogadro number, V is the volume of the unit cell, and n is the number of sites per unit cell. On the other hand, the expression for the pycnometric density, ϱ_P, given below is obtained by dividing the total mass of the specimen by its volume,

$$\varrho_P = \frac{\left(N_A^\alpha M_A + N_B^\beta M_B\right)/N_0}{V \times (N_s/n)} , \qquad (2)$$

where N_A^α is the number of A atoms on the α-sublattice sites and N_B^β that of the B atoms on the β-sublattice sites. The difference between these two densities is

$$\varrho_x - \varrho_P = \frac{\left(N_v^\alpha M_A + N_v^\beta M_B\right)/N_0}{V \times (N_s/n)} . \qquad (3)$$

For the case of the rare-earth disilicides, we assume that vacancies exist only on the β-sublattice, i.e. the sublattice sites occupied by the Si atoms. By manipulating the above equation and taking N_v^α to be 0, we obtain the vacancy concentration as

$$z = \frac{N_v}{N_s} = \frac{\varrho_x - \varrho_P}{M_B} \times \frac{N_0 V}{n} . \qquad (4)$$

Figure 1 shows the X-ray-diffraction patterns of the four disilicides of Y, Dy, Ho and Er. The lattice parameters obtained using both the Nelson and Riley and Cohen methods [18–20] are given in Table 1. Although the precision of the lattice parameters obtained is ±0.00001 nm, we estimate the uncertainty to be ±0.0001 nm.

As shown in Table 1, the uncertainties in the measured vacancy concentrations are due primarily to those in the measured bulk densities. The densities obtained from the X-ray data are of much higher accuracy. While the uncertainties in the volume measurements to obtain the densities from the pycnometer are the same, those in the measured densities depend on the sample s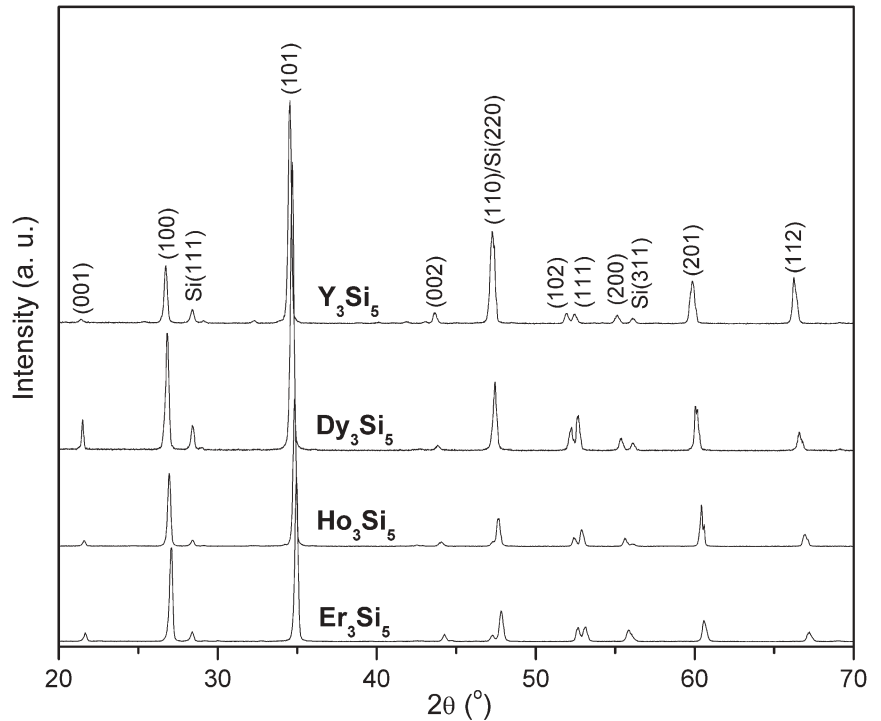ize. In view of the larger densities of Er, Ho and Dy disilicides in comparison to that of Y disilicide the later sample size is three times larger, thus reducing the uncertainties in the measured densities of YSi$_{1.67}$.

FIGURE 1   X-ray patterns of the disilicides of Dy, Er, Ho and Y
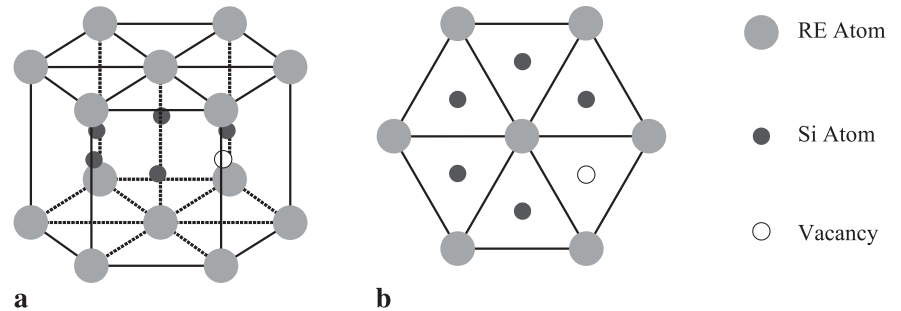

a   b

FIGURE 2   **a** A unit cell of RESi$_{1.67}$ showing that one of the six Si atoms is missing. **b** Top view of the unit cell

Compound	Lattice constants		ϱ_x (g/cm³)	ϱ_P (g/cm³)	$z = N_v/N_s$ (%)
	a (nm)	c (nm)			
YSi$_2$	0.38415	0.41425	4.5525	4.2515 ± 0.01	11.4 ± 0.4
DySi$_2$	0.38285	0.41230	6.9400	6.6390 ± 0.06	11.3 ± 2.4
HoSi$_2$	0.38100	0.41035	7.1190	6.7755 ± 0.05	12.7 ± 1.8
ErSi$_2$	0.37990	0.40895	7.2610	6.9330 ± 0.05	12.0 ± 1.9

TABLE 1   Lattice parameters and densities of the disilicides

ties of the measurements. The chemical composition of the RE disilicides is close to RESi$_{1.67}$, i.e. one of the six sites normally occupied by Si atoms on the silicon sublattice becomes vacant as shown in Fig. 2.

4   Conclusion

In summary, we conclude that the data obtained agree with the theoretical vacancy concentration of 11.1% per mole of RESi$_2$ within the uncertain-

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