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Contact reaction between Si and rare earth metals

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Reactions between Si and thin films of rare-earth metals (Gd, Dy, Ho, Er, plus Y and La) in the temperature range of 275–900 °C have been studied by using x-ray diffraction and ion backscattering spectrometry. The disilicides of these metals are apparently the first phase to form, forming rapidly within a narrow temperature range (325–400 °C), and are stable up to 900 °C. The growth does not follow a layered growth mode.

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Reactions between transition metals and silicon have been studied quite systematically with many interesting and desirable properties being reported.¹ The study of the rareearth metals in the same manner has just been published.^{2,3} The impetus was that of gaining a broader picture of silicide formation, as they have been found to be technologically important for contacting silicon in integrated circuitry. Device sizes are continuing to shrink, thereby making the contact characteristics (and therefore silicide properties) even more important in the overall device characteristics. We found that the rare-earth silicon reaction produced silicides that had a number of very interesting and important properties.

The rare-earths studies (Ce, Gd, Dy, Ho, Er,³ plus Y, Ref. 3, and La) were deposited by electron-gun evaporation onto buffered HF-cleaned bare (100) Si wafers to a thickness of approximately 2000 Å at rates of about 10 Å/sec. The substrate temperature was maintained at 100 °C during deposition. These were examined and then annealed for times ranging from 5 min to several hours in a resistance furnace containing a flowing He atomosphere at temperatures ranging from 275 to 900 °C. Oxygen was filtered out by passing the He atmosphere over a bed of Ti held at 900 °C. This reduced the estimated oxygen partial pressure to near 10^{-9} Torr. Still, the severe oxidation problem forced us to anneal the wafers face down on an unspecified sapphire wafer and bury them with chips of another wafer of the same material to prevent oxidation.

The four-point probe and electron microprobe were used to characterize the impurity levels of the films both before and after annealing. No impurity other than oxygen was observed (i.e., content < 0.1 wt. %), and the oxygen impurity level (<2 w/o) was consistent with the existence of a 20–100-Å native oxide film. Seeman-Bohlin x-ray diffraction was used to identify phases and structures, while MeV He⁺ ion backscattering was used to obtain compositional profiles with respect to depth.

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We found that all the metals studied reacted with silicon at temperatures lower than 400 °C in less than 30 min to form disilicides as a first and apparently last phase. These were found to be stable up to 900 °C and appear as very stable compounds on the few rare-earth-Si phase diagrams that are available (i.e., Ce-Si, Y-Si, U-Si, Th-Si).⁴ Moreover, these disilicides had a very uniform and sharp interface with the underlying Si as observed from their backscattering spectra. Figure 1 shows the backscattering spectra of an Er film before and after annealing at 400 °C for 15 min. Figure 2 shows the x-ray diffraction spectrum of this reacted film. Most of the reflections can be identified as those of the disilicide. We found occasional oxide reflections despite our efforts to prevent oxidation, though they were generally quite weak when they did appear. The temperature range of the reaction $(\sim 30 \text{ °C})$ was surprisingly narrow for the time for complete reaction to vary from around $\frac{1}{4} - \frac{1}{5}$ h to several hours. Annealing at even lower temperatures yet produced no detectable interfacial reactions within any reasonable time period (days).

Both the ion backscattering and optical microscope studies indicated that the disilicide nucleated in a few spots and then grew as isolated islands. See Fig. 3 for an optical





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FIG. 2. Seeman-Bohlin x-ray diffraction spectrum of a 2000-Å Er film on Si after annealing 15 min at 400 °C.

picture of the morphology of a partially reacted sample demonstrating this behavior. The ion backscattering spectra also demonstrate this by being sensitive to the position of the beam on the partially reacted samples. It was possible to obtain spectra ranging from nonreacted to fully reacted just by moving the beam across the sample.

Table I summarizes the annealing conditions, the results of the annealings, the crystal structures, melting points, and the measured sheet resistivity of both the metals and their disilicides. We note that the as-deposited resistivities are about a factor of 2 higher than the corresponding bulk values and the comparison of the metal, and its disilicide demonstrates that the disilicides are good electrical conductors.

The observation of disilicides as first phase to form is similar to the refractory metals (Cr, Mo, W, V, Nb, and Ta),⁵⁻¹⁰ but the reaction temperature is about 200 °C lower, and the temperature range of formation is much narrower. The growth modes of these two kinds of disilicides are quite different also; the refractory follows a layered growth¹, while the rare-earth does not. Also the observed growth mode here is very different from that of HfSi₂ (Ref. 11) or NiSi₂¹². The growth of HfSi₂ was shown by the backscattering spectra as a uniform lowering of the hf signal with respect to depth, which is not found here. The case of NiSi₂ has a very rough



FIG. 3. Optical micrograph $(50 \times)$ of surface of Ho film annealed 2 h at 350 °C. Dark areas are $HoSi_2$ and are sticking up out of the remaining Ho (white).

interface with the Si wafer after the reaction, quite unlike the sharp interface we have observed here.

Because the formation temperature range is narrow and the growth is not layered, we were unable to determine either the kinetic rate or activation energy that limits the reaction with techniques we used. Whether the reaction is nucleation or growth limited is an interesting question that will require a more extensive investigation for clarification.

Another interesting aspect of the narrow range of reaction temperatures is that they show no dependence on the melting point of the metal, which varies from 795 °C for Ce to 1497 °C for Er. On the other hand, the melting point of the disilicides are much closer together as can be seen in Table I. These melting points are high, and they indicate that their free energy of formation will be high giving a large driving force for their formation. This is also indicated by the rare earths (also Y and La) having two s valence electrons such that the disilicide should be a very stable compound.

The above energetic considerations of the disilicide formation are independent of the melting point of the metals. However, the melting point of the rare earths and of Si are closely related to the eutectic temperatures in the rare-earth-Si binary systems. For example, the lowest-temperature eutectic in the Ce-Si system is next to Ce, but it is next to Si in the Y-Si system. The same is also true for U-Si and Th-Si

Table I. Summary of annealing results of rare-earth metals of Si.

Element	Ce	Gd	Dy	Ho	Er	Y	La
Structure	bcc	Hex	Hex	Hex	Hex	Hex	Hex/cu
mp (°C)	795	1312	1407	1461	1497	1509	920
Resistivity							
(Ω / \Box)		6.65	5.8	4.97	2.76	4.75	5.2
Annealing	400-1 h	300 - > 1 h	325-2.5 h	350->2 h	350->24 h	325- > 8 h	< 275-1 h
temps and	500-1 h	- < 2 h	350-1 h	- < 4 h	375-75 min	350->1 h	
times		325- < 30 min		375-45 min	400-15 min	375-45 min	
Disilicides	CeSi ₂	GdSi ₂	DySi ₂	HoSi ₂	ErSi ₂	YSi ₂	LaSi ₂
Structure	Tetra	Ortho	Ortho	Hex/Ortho	Hex	Hex/Ortho	Tetra
(Ω / \Box)	•••	6.6	6.5	5.9	2.44	4.3	3.7
mp (°C)	1620	2100	1550		•••	1635	1580

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respectively (the others with known phase diagrams).⁴ Hence if we follow the amorphous membrane model assuming a composition near the lowest-temperature eutetic point, as proposed by Walser and Bene¹³ to predict disilicide formation, we find it predicts correctly only for the rare-earth metals with a melting point higher than Si.

Although the driving force for disilicide formation is expected to be large, the finding of formation temperatures below 400 °C is quite surprising from a kinetic point of view. This is because no transition metal disilicides have been found to form at such low temperatures, a continuous supply of Si is needed for the formation, and just how can the covalent bonds of Si be broken at such low temperatures? We recall that near-noble metals can react with Si at around 200 °C, forming metal rich silicides such as Pd₂ Si. There metal atoms have been found to dominate the diffusion during the silicide growth, and a mechanism which invokes metal interstitials to weaken the covalent bonds in Si has been proposed to explain the low-temperature reaction.¹⁴ The kinetic mechanism which leads to the formation of rare-earth disilicides is not at all clear yet though.

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Influence of the electric field on collection efficiencies of solar cells

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Solar cells which show a field-dependent collection efficiency in the current saturation range must exhibit a field-dependent carrier redistribution over localized states within the junction. Such redistribution may be caused by "field quenching" which is a well-known effect in photoconductive CdS, providing for field saturation and consequently causing the short-circuit current to saturate before the emitter limit is reached.

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It is a well-known fact that in a variety of solar cells the current collection efficiency increases with the electric field in the junction, as inferred from the junction capacity and the applied voltage. This behavior is observed in heterojunctions which have significant interface recombination.

A model was recently proposed¹ which seems to explain such relationship on the basis of competition between interface recombination and drift away from the locus of recombination. This model, however, does not take into consideration that the field in an ordianry junction (i.e., with fieldindependent carrier-generation rates) increases with increased reversed bias²; hence one expects a further increase in current. In contrast to this expectation, the current is often found to saturate in these cells.

On the other hand, capacitance measurements (with $C(V) \simeq \text{const}$) and field-dependent collection efficiencies

(however, with $j(V) \simeq \text{const}$) indicate indeed a limited field F_j at the emitter/junction interface (with $F_j(V) \simeq \text{const}$) in the saturation range. This must then be taken as direct evidence for the existence of a mechanism which limits the field within the junction. Such a field limitation cannot be caused by a simple doping profile: Constant doping causes an increase of $F_j \sim (V)^{0.5}$; a steplike doping with almost complete compensation near the emitter/junction interface could simulate field saturation at a given bias, but causes an increase of $F_j \sim V$ with increasing reverse bias (Fig. 1). Hence the collection efficiency and therefore the current is expected to increase and not to saturate.

In order to achieve a constant F_j one must assume a *field-dependent* space-charge reduction as indicated in Fig. 2. It can be produced by field-induced release of the trapped space charge, commonly referred to as field quenching.³

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