# Epitaxial yttrium silicide on (111) silicon by vacuum annealing

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Epitaxial $YSi_{2-x}$ films have been fabricated. The smooth 430-Å-thick silicide films on Si (111) substrates were characterized by a Rutherford backscattering minimum channeling yield $\chi_{min} = 8\%$, establishing $YSi_{2-x}$ as one of the best known epitaxial silicides. Results of electrical measurements are also presented.

Interest in epitaxial silicides[1] is increasing rapidly, in part because of the opportunities these materials provide for fundamental study of metal-semiconductor interfaces, and in part due to the promise they hold for Si-based electronics. Some two dozen silicides are known to form epitaxially on Si.[2,9] Although all these silicides are called "epitaxial," some are, so to speak, more epitaxial than others. Arbitrarily defining these "more epitaxial" silicides as those which form single-crystal epitaxial layers characterized by a minimum channeling yield $\chi_{min} \leq 10\%$ (perfect single crystals typically give $\chi_{min} \sim 3\%$), we would be left with just four, all known for over ten years: PtSi, $NiSi_2$, $CoSi_2$, and $Pd_2Si$. In this letter we describe the work which led to the addition of a new member to this small group, namely, $YSi_{2-x}$/Si (111).

Thin-film rare-earth (RE) silicides, in which we also include yttrium, have been studied for the last six years, beginning with the pioneering work of Baglin *et al.*[3] All of them were found to form in a characteristic fashion. Metallic RE film deposited on Si, when heated in a furnace, does not react with Si layer by layer; instead, there is a time delay followed by a sudden onset of a very rapid reaction.[4] This behavior suggested[5] the presence of an inhibiting contaminant surface barrier (oxide, carbide[6]) on the Si substrate which has to be penetrated in order to form the silicide. It has been shown that Si rather than metal atoms are moving during the reaction.[7] The barrier tends to be pierced in local regions; Si quickly diffuses through the pinhole and moves laterally into the growing silicide layer, thus forming a pit in the silicon substrate. Morphologically poor, pitted surfaces have always been found in furnace annealed RE silicides, unless special care was taken to clean the Si surface in ultrahigh vacuum[7,8] or to break the surface barrier by means of ion beam irradiation.[8]

An improvement over traditional furnace annealing results has been achieved by Knapp, and Picraux[9] who prepared RE silicides using an unconventional technique involving rapid electron beam heating to high temperatures (1500–1700 °C). They observed improved morphology and evidence of limited epitaxy in a number of RE silicides, with the best $\chi_{min} = 26\%$ found for the Y silicide.[9] Indeed, the hexagonal $YSi_{2-x}$ ($AlB_2$ structure which has $C32$ symmetry) is essentially a perfect lattice match to Si (111).[9] The Si deficiency, as determined in Rutherford backscattering, was in the range of 15 to 20% yielding $YSi_{1.6-1.7}$.[3,9] Based on transmission electron microscopy (TEM) evidence, Knapp and Picraux further suggested[10] that in a Si ring one out of six Si atoms is missing (i.e., $x \simeq 0.33$), and that vacancies are ordered into a superlattice.

We decided to investigate the limits of conventional furnace annealing techniques which had previously failed to produce any yttrium silicide epitaxy. To our surprise, we obtained epitaxial $YSi_{2-x}$ of unsurpassed quality characterized by $\chi_{min} = 8\%$, good morphology, and a smooth silicon/silicide interface (Figs. 1 and 2). The samples were studied with Rutherford backscattering (RBS), transmission electron microscopy (TEM), and various electrical measurements.

Oriented Si(111) $\pm 0.5°$ *n*- and *p*-type ($\rho \simeq 2$–$3\ \Omega$ cm) wafers received standard cleaning (P-clean) followed by growth of $\sim 1000$ Å of $SiO_2$ in dry oxygen. The oxide was then stripped, and the wafers cleaned using the Shiraki technique[11] to reduce carbon contamination and avoid formation of the inhibiting barrier which, according to Ref. 6, consists of carbides rather than oxides of Si. The wafers were then spin dried and loaded inside a magnetron sputtering system,[12] where Y films 300 Å thick were sputtered from a high-purity Y target[13] at a deposition rate of 10 Å/s. The oil diffusion pumped sputtering chamber is equipped with a liquid-nitrogen shroud and can be pumped to a base pressure of $\sim 3 \times 10^{-8}$ Torr. Sputtering is performed in 15 mTorr of research purity Ar and the partial pressure of all impurity gases ($H_2O$, $O_2$, $N_2$, etc.) during the deposition has been estimated at $\sim 2 \times 10^{-7}$ Torr.[12] Si wafers covered with Y were then loaded into a vacuum furnace. The vacuum annealing system consists of the furnace *per se* and a long evacuated quartz tube over which the furnace can slide back and

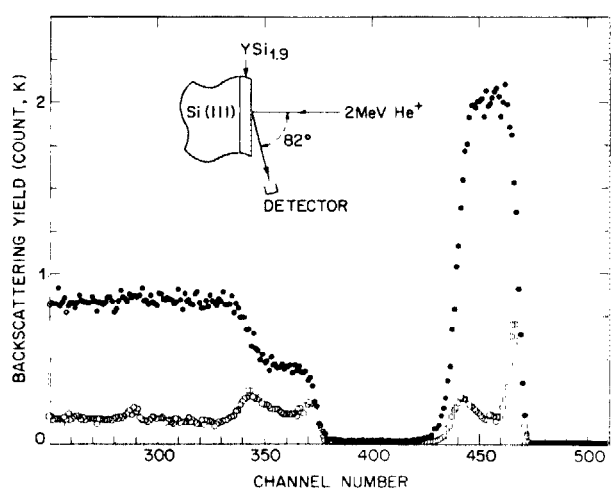


FIG. 1. RBS and channeling spectra for sample 111-5. Closed circles are the random spectrum and open circles are the ⟨111⟩ axial channeling data; $\chi_{min} = 7.7\%$ beneath the surface peak of Y.

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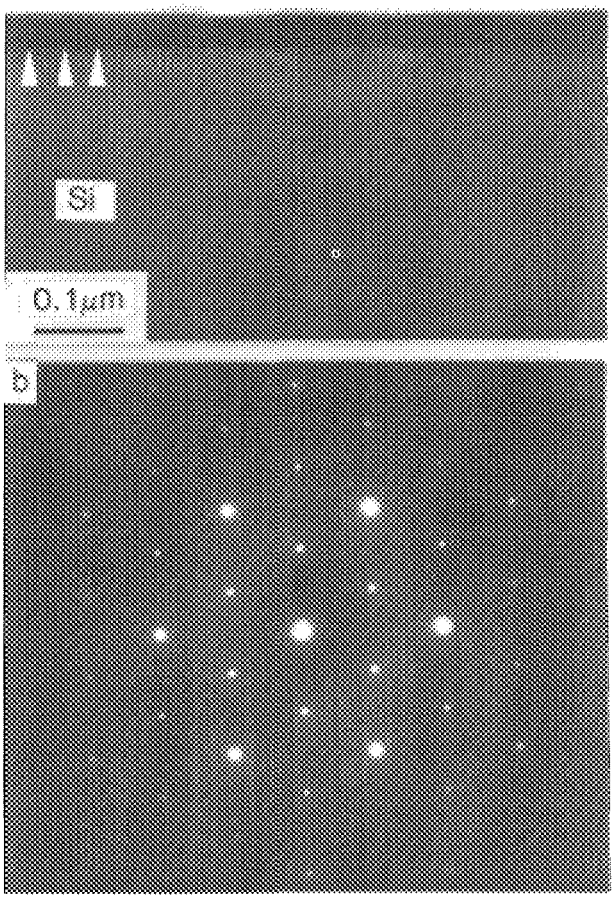


FIG. 2. (a) Cross-sectional TEM; the $YSi_{2-x}$/Si interface is marked with arrows, and (b) electron diffraction pattern of $YSi_{2-x}$ (sample 111-5). No misfit between Si (111) and $YSi_{2-x}$ can be detected.

forth. First the tube was outgassed for several hours at 1000 °C together with a small box made of Zr foil which was placed inside the tube on a movable quartz holder (Zr is well known as a getter of $O_2$). The samples were then loaded into the loosely closed Zr box, and the tube was again evacuated. At this point the furnace was allowed to reach the desired annealing temperature with the samples positioned away from the hot region of the tube. Using a magnetic coupling the samples in the Zr box were then driven into the hot region of the tube. The vacuum during anneals was consistently better than $1\times10^{-8}$ Torr. Best results were obtained with two-stage anneals; one hour at 475 °C followed by one hour at 900 °C. RBS measurements showed that the 900 °C anneal serves to drive off oxygen from the silicide film and improve epitaxy. The samples were then withdrawn from the hot region of the tube and removed for structural and electrical characterization.

The overall epitaxial perfection of thin $YSi_{2-x}$ layers was analyzed by RBS and channeling using 2 MeV helium ions. Shown in Fig. 1 are ⟨111⟩ axial channeling (open circles) and random (close circles) RBS spectra of a thin $YSi_{2-x}$ layer. A glancing exit angle was used to increase the depth resolution. The channeling minimum yield, which is a good measure of the overall crystallinity of the thin layer, is $\chi_{min} = 7.7\%$ just beneath the surface peak of the yttrium signal. There is observable dechanneling across the thickness of the silicide film. The surface peaks are probably due to oxidation. Analyses of the random spectrum using tabulated energy loss data for the individual elements yield a stoichiometry of $YSi_{1.9}$ for this particular thin film. We consider this number to be reliable to $\pm$ 10%, i.e., the stoichiometry may be anywhere from $YSi_{1.7}$ to $YSi_{2.0}$. However, the possibility that our films have fewer Si vacancies than reported previously[3,9,10] is supported by our TEM and resistivity results described below.

Films with $\chi_{min} \simeq 8\%$ appear continuous and reasonably smooth in the optical microscope. TEM supports this conclusion. Figure 2(a) shows the (211) cross-sectional view of a $YSi_{2-x}$ layer on a Si substrate. The $YSi_{2-x}$/Si interface is marked with three white arrows. It is seen that the silicide layer is quite uniform in thickness and free of pinholes, a fact confirmed by plan-view TEM imaging. Hence we have no reason to think that RBS determination of stoichiometry suffers from counting extra Si signal from the substrate exposed through pinholes. A further examination of the silicide layer has revealed that the silicide has the expected hexagonal crystal structure and contains faultings lying in the film plane, which is the (0001) basal plane. Figure 2(b) is the electron diffraction pattern of the $YSi_{2-x}$/Si composite examined from the film normal direction. Although this pattern consists of both hexagonal (0001) $YSi_{2-x}$ and diamond cubic (111) Si patterns, no separation of the spots is detectable, indicating that there is practically no misfit. This result is consistent with previous observations made by Knapp and Picraux.[9,10] In addition, the epitaxial relationship between $YSi_{2-x}$ and (111) Si is (0001) $YSi_{2-x}$ ‖(111)Si and $[10\bar{1}0]$ $YSi_{2-x}$ ‖$[\bar{1}\bar{1}2]$ Si. We note that in agreement with the RBS determination of the near-stoichiometric composition $YSi_{1.9}$, we see no evidence for a large number of ordered Si vacancies. Plan-view microscopy of the (0001) $YSi_{2-x}$/(111)Si composite layer revealed that the silicide film was a single crystal of $YSi_{2-x}$ with occasional small patches of differently oriented grains. Faintly visible lines in the micrographs were associated with defects connected to the ends of faults observed in the cross section.

Electrical measurements were performed on two samples: 111-5, one of the best samples with $\chi_{min} = 8\%$, and an earlier "generation" sample $\delta$, $\chi_{min} = 30\%$, which was prepared without Shiraki cleaning, and treated in a vacuum of $\sim5\times10^{-8}$ Torr without a Zr enclosure at 975 °C for 1 h. Table I lists a number of measured parameters for these two samples.

Our temperature-dependent resistivity measurements indicate that $YSi_{2-x}$ has a $T^5$ power law dependence of the form $\rho(T) = \rho(0) + AT^5$ in the temperature range $T \simeq 0$–30 K. This is typical of simple *s-p* metals and is, for example,

TABLE I. Characteristics of the two representative samples.

| Sample | One hour anneals 1st (°C) | One hour anneals 2nd (°C) | $d$ silicide (Å) | $\chi_{min}$ (%) | $\rho(293\ K)$ ($\mu\Omega$ cm) | $\rho(4.2\ K)$ ($\mu\Omega$ cm) | $Z^a$ | $A^a$ ($\times 10^{-8}$ $\mu\Omega$ cm/K$^5$) | $\Delta\rho/\rho_0$ at 0.3 K 10 T | $n_{Hall}$ ($\times 10^{22}$ cm$^{-3}$) | $(\rho L)_{f.e.}$ ($\mu\Omega$ cm Å) | $\phi$ to $n$-Si (eV) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 111-5 | 475 | 900 | 430 | 8 | 49.4 | 16.5 | 5[b] | 1.07[b] | 0.1 | 2.7 | 1430[d] | 0.36 |
| $\delta$ | 975 | ··· | 420 | 30 | 75 | 41 | 5[c] | 0.92[c] | 0.006 | ··· | ··· | 0.36 |

[a] $Z$ and $A$ are the parameters in the expression $\rho(T) = \rho(0) + AT^Z$, where typically $T \lesssim 0.1\theta_{Debye}$.
[b] Values of $Z$ and $A$ for $4.2 < T < 28.3$ K.
[c] Sample $\delta$ shows a small resistivity minimum at 11 K. The quoted values of $Z$ and $A$ are given for $15.5\ K < T < 25$ K.
[d] The free-electron value calculated using $n_{Hall}$.

similar to the temperature dependence we have found for $CoSi_2$. The residual resistivity, which characterizes the amount of static disorder, is relatively high even in our best samples [$\rho(4.2\ K) = 16.5\ \mu\Omega$ cm], presumably due to Si vacancies. Similar residual resistivities found in $NiSi_2$ and $TaSi_{2.5}$ are believed to arise from intrinsic nonstoichiometry.[14] The electron-phonon resistivity in $YSi_{2-x}$, $\rho_{e-ph}(293\ K) \simeq 33\ \mu\Omega$ cm (Table I), is a factor of 3 higher than in $CoSi_2$ and $NiSi_2$.[14] Note also that the room-temperature value of resistivity in our best samples (49.4 $\mu\Omega$ cm) is about three times lower than the corresponding value which can be deduced from the data on nonepitaxial yttrium silicide given in Ref. 4. Hall measurements indicate electrons are the dominant charge carrier involved in transport, with a concentration $n_{Hall} = 2.7 \times 10^{22}$ cm$^{-3}$. Using this value of $n$ to calculate $\rho L$ gives $L = 87$Å at 4.2 K in sample 111-5, where $L$ is the free-electron mean free path. The observation of relatively strong magnetoresistance in the sample with $\chi_{min} = 8\%$ is evidence for multiple bands and/or anisotropy in the Fermi surface. However, the suppression of this magnetoresistance by a factor of more than 15 in the more disordered sample with $\chi_{min} = 30\%$ is probably related to disorder-induced smearing of electronic states at the Fermi surface. The measured Schottky barrier height of 0.36 eV on $n$-type silicon was found to be in agreement with the literature on rare-earth silicides.[15] Finally, both $YSi_{2-x}$ samples were nonsuperconducting down to a temperature of 0.3 K.

In conclusion, we have prepared the best epitaxial yttrium silicide reported so far; in fact $YSi_{2-x}$ ($x \simeq 0.1$) is one of the highest quality epitaxial silicides in existence. This publication should be viewed as an existence proof for epitaxial Y silicide formation with $\chi_{min} < 10\%$ rather than an optimization study. Clearly, *in situ* work using an ultrahigh vacuum system would be desirable. We note that our surface preparation and annealing techniques may be useful in improving the epitaxial quality of other silicides.

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