Epitaxial ternary $Re_xMo_{1-x}Si_2$ thin films on Si(100)

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Reactive deposition epitaxy was used to synthesize thin layers of $Re_xMo_{1-x}Si_2$ on Si(100). In the case of $x=1$, $ReSi_2$ layers of excellent crystalline quality have been reported previously [J. E. Mahan, K. M. Geib, G. Y. Robinson, R. G. Long, Y. Xinghua, G. Bai, and M.-A. Nicolet, Appl. Phys. Lett. **56**, 2439 (1990)]. In the case of $x=0$, however, virtually no alignment of the $MoSi_2$ and the substrate is found, although this silicide is nearly isomorphic to $ReSi_2$. For intermediate values of x, highly epitaxial ternary silicides are obtained, at least for a Mo fraction up to 1/3.

I. INTRODUCTION

During the last decade, transition metal silicides have been the object of a vast number of fundamental studies. Most of the effort has been devoted to the investigation of the metallic phases such as $CoSi_2$, $NiSi_2$, and $TiSi_2$. However, semiconducting silicides such as β-$FeSi_2$, $CrSi_2$, and $ReSi_2$ have received more and more attention.[1] Among these semiconducting silicides, $ReSi_2$ is of special interest due to its very narrow band gap (0.12 eV or, equivalently, 10.4 μm).[2] The applications foreseen include the creation of infrared detectors for operation in the 8–14 μm bands of atmospheric transparency.

Forming a ternary silicide phase from this semiconducting material, and an isomorphic (semi-)metallic silicide might make it possible to further decrease the band gap and hence extend the photoresponse of a detector to even longer wavelengths. A possible candidate that fulfills these two conditions for $ReSi_2$ is semi-metallic $MoSi_2$.[3]

$ReSi_2$ has a body-centered orthorhombic lattice structure in which the a and b lattice parameters have nearly the same value ($a=3.1289$ Å and $b=3.1434$ Å).[4] This structure is very nearly that of the body-centered tetragonal C11 type, referred to as the $MoSi_2$ structure. In the following, it will be assumed that $ReSi_2$ possesses a body-centered tetragonal lattice. $MoSi_2$ only possesses this tetragonal lattice structure when formed above a transition temperature of 600 °C. Below this temperature, it has a $CrSi_2$ hexagonal C40 structure type.[5] Table I summarizes the lattice constants of $ReSi_2$ and $MoSi_2$,[4] together with their lattice mismatch with respect to Si(100). The latter values have been recalculated using the new lattice parameters of Ref. 4, following the procedure of Zur *et al.*[6] They differ slightly from those previously published.[1] As seen from this table, $ReSi_2$ and $MoSi_2$ are not only isomorphic, but they also have very similar lattice constants.

Ternary silicides of $ReSi_2$ and the high-temperature form of $MoSi_2$ were suggested as early as 1965.[7] More recently, Long *et al.* have synthesized polycrystalline $Re_xMo_{1-x}Si_2$ films on Si(100) using sputtering from a Re_xMo_{1-x} target.[8] From the gradual shift of several x-ray diffraction peaks with a changing Re/Mo ratio, it was concluded that $Re_xMo_{1-x}Si_2$ ternaries are formed (complete solubility), rather than two-phase mixtures of binary silicides (phase separation). With x ranging from 0 to 1, a continuous variation in both optical (infrared reflectance and transmittance) and electrical (room-temperature resistivity) properties was observed. By changing the Re/Mo ratio of the ternary, it should be possible to gradually vary the silicide band gap to any value between 0 and 0.12 eV, thus achieving band gap engineering in the far infrared region. For the best quantum efficiency, epitaxial $Re_xMo_{1-x}Si_2$ layers will probably be required. Our initial investigation of reactive deposition epitaxy of these ternaries is described in Secs. II and III.

II. EXPERIMENTAL PROCEDURES

The depositions were performed in an ultrahigh vacuum chamber (the vacuum was typically in the 10^{-9} Torr range during deposition), equipped with two e-guns. As source materials, high purity Re (99.99%) and high purity Mo (99.95%) pellets were used. Prior to deposition, the Si(100) wafers were dipped in a 10% HF+NH_4F solution for 30 s, after which they were loaded into the vacuum chamber, and subsequently held for 5 min at 200 °C and 15 min at 400 °C. Finally, the substrate was exposed briefly to a Si beam for removal of native oxide at a wafer temperature of 800 °C, followed by metal deposition at a selected substrate temperature.

Phase identification was done by *ex situ* x-ray diffraction in Bragg–Brentano geometry, using a Cu $K_{\alpha 1}$ source ($\lambda=1.540593$ Å). The composition of the layers, their thickness, crystalline quality, and interface with the substrate were studied by MeV $^4He^+$ backscattering and channeling spectrometry.

III. RESULTS AND DISCUSSION

Reactive deposition epitaxy consists of deposition of a metal onto a hot Si wafer, thus allowing an immediate reaction of the metal with the substrate. This technique has

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TABLE I. $ReSi_2$ and $MoSi_2$ lattice parameters[a] and mismatch with respect to Si(100).

	a (Å)	c (Å)	Mismatch ⟨100⟩	Mismatch ⟨010⟩	Common unit mesh (Å²)
$ReSi_2$	3.1362[b]	7.6743	−0.08%	+2.08%	120.4
$MoSi_2$	3.2050	7.8479	+2.18%	+4.32%	125.8

[a]See Ref. 4.
[b]The $ReSi_2$ lattice is considered to be tetragonal; the tabulated lattice parameter a is the mean value of the orthorhombic lattice constants a and b.

been shown[9] to be very effective for the growth of epitaxial rhenium silicides: after deposition of about 500 Å Re on a Si(100) substrate held at 650 °C, a $ReSi_2$ film with a very sharp interface to the substrate and a minimum yield for channeling as low as 2% was obtained (Fig. 3 in Ref. 9).

A. Reactive deposition of Mo

Using the same strategy as in the case of $ReSi_2$ formation described in Ref. 9, we studied silicide formation during Mo reactive deposition epitaxy. The substrate temperature during deposition was always kept at or above 600 °C in order to form only the tetragonal phase of $MoSi_2$, which is the structure of interest in the formation of ternary $Re_xMo_{1-x}Si_2$. Indeed, x-ray diffraction indicates that the latter structure is the only phase present in the as-deposited samples.

At all deposition temperatures used (ranging from 600 to 800 °C), a continuous $MoSi_2$ layer with an abrupt interface to the substrate was formed, as was deduced from backscattering measurements. As an example, Fig. 1 shows the spectrum of a Si substrate on which 500 Å of Mo was deposited at 700 °C. However, from the spectrum taken in Si⟨100⟩-aligned geometry, it can be seen that almost no channeling occurs in the silicide layer. The observed minimum yields varied between 95% and 100% for the different deposition temperatures, indicating that there is poor epitaxial alignment between the silicide and the substrate.

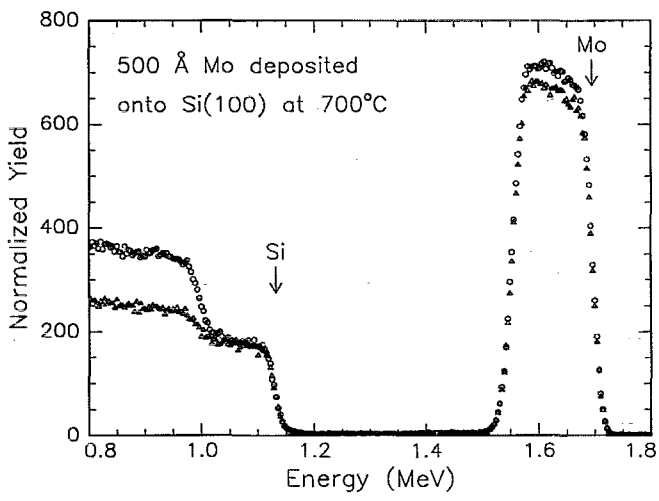

FIG. 1. 2.0 MeV ^4He backscattering spectra of 500 Å of Mo deposited on Si(100) at 700 °C: (○) random beam incidence (7° off sample normal) and (△) channeled in the Si⟨100⟩ direction. The scattering angle of the detected particles is 170°.

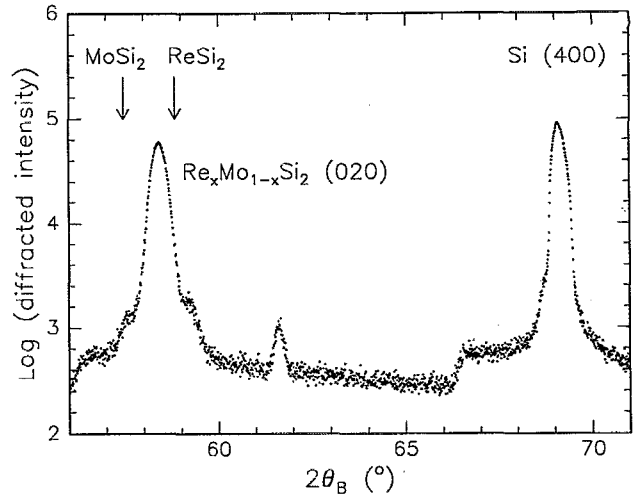

FIG. 2. X-ray θ–2θ diffraction of Re_xMo_{1-x} deposited onto Si(100) at 650 °C for $x=0.82$. The arrows indicate the 2θ values for the two binary silicides. The peak at $2\theta \approx 61.5°$ and the absorption edge at $2\theta \approx 66.5°$ are artifacts caused by a Ni filter used in the experiment.

In an attempt to enhance the crystallinity of the $MoSi_2$ layers, the samples were further annealed *ex situ* in a vacuum furnace (5×10^{-7} Torr) at 1100 °C for 30 min. This subsequent annealing did not result in a noticeable change of the crystalline quality; the channeling minimum yield only dropped a few percent. On the other hand, the initially continuous $MoSi_2$ layers started to break up into islands when exposed to a temperature of 1100 °C for 30 min. We believe that this lack of an epitaxial orientation is due to the larger lattice mismatch of the $MoSi_2$/Si(100) system, compared to that of $ReSi_2$/Si(100) (see Table I).

B. Reactive deposition of Re_xMo_{1-x}

Knowing the behavior of both end points ($MoSi_2$ and $ReSi_2$), we then studied the silicide formation when the two metals were deposited simultaneously onto a hot substrate. Re and Mo were co-deposited at a constant Re_xMo_{1-x} ratio onto a Si(100) substrate that was kept at 650 °C, the optimum temperature for the formation of epitaxial $ReSi_2$.[9] In order to minimize the lattice mismatch with the Si substrate and thus enhancing the chances for epitaxial growth, Re/Mo flux ratios larger than unity were initially selected.

As was the case for sputtering from a Re/Mo target,[8] a homogeneous $Re_xMo_{1-x}Si_2$ ternary can be formed with reactive co-deposition. Indeed, x-ray diffraction (see Fig. 2 for $x=0.82$) confirmed the formation of a ternary silicide, as indicated by the gradual shift of the (020) silicide peak from the $ReSi_2$ position towards the $MoSi_2$ position, as the Mo fraction is increased. We found that co-evaporation (or co-sputtering) is essential to obtain these ternaries. Subsequent reactive deposition of Re and Mo, on the other hand, results in the phase separation of $ReSi_2$ and $MoSi_2$.

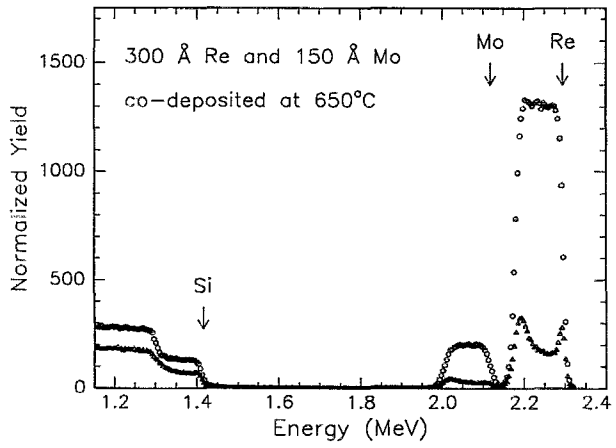

FIG. 3. 2.5 MeV ^{4}He backscattering spectra of Re_xMo_{1-x} deposited onto Si(100) at 650 °C for $x=0.68$: (○) random beam incidence (7° off sample normal) and (△) channeled in the Si⟨100⟩ direction. The scattering angle of the detected particles is 170°.

The composition and thickness of the ternary silicides were determined by backscattering spectrometry (see Fig. 3, the results are summarized in Table II). From these measurements, it can be concluded that the interface sharpness between the silicide and the substrate is within the backscattering depth resolution (less than 50 Å when tilting the sample over a large angle with respect to the incoming beam). To obtain information on the crystalline quality of the ternaries, backscattering spectroscopy in channeling geometry was performed. The spectrum taken in Si⟨100⟩-aligned geometry is shown in Fig. 3. From these data, minimum yield values for both the Mo and the Re signals are calculated (Table II). Both Re-rich layers reported here exhibit a good epitaxial alignment to the substrate, whereas poor alignment was observed in the case of the Mo-rich layer. The high minimum yield in the Si signal (see Fig. 3) does not indicate that the Si sublattice is disordered, rather, it is due to the large difference in atomic number between Si and the two metals.[10] It is interesting to note that even with a Mo fraction as high as $\frac{1}{3}$, a minimum yield of only 11%–12% is still obtained. To the best of our knowledge, this is the first observation of an epitaxial $Re_xMo_{1-x}Si_2$ structure.

From the values of the lattice mismatches, one would expect a better crystallinity (hence a lower minimum yield) for higher x values. Although a poor alignment of the epilayer is found for small Re/Mo flux ratios (i.e., see $x=0.34$ in Table II), the crystalline quality does not scale monotonically with x. Apparently, other factors also play a role in the crystallinity of the ternary silicide, the origins of which have yet to be elucidated.

TABLE II. Basic compositional and structural parameters of the samples reported in this article.

	x	Thickness (Å)	χ_{min} (Mo)	χ_{min} (Re)
$MoSi_2$	0.00	1350	95%	–
$Re_xMo_{1-x}Si_2$	0.34	1800	82%	80%
$Re_xMo_{1-x}Si_2$	0.68	1100	12%	11%
$Re_xMo_{1-x}Si_2$	0.82	2600	23%	15%
$ReSi_2$	1.00	1500	–	2%

From a combination of x-ray data and backscattering spectra, information on the strain of the silicide layers can be obtained. The composition of the layers is known from the backscattering experiments with random beam incidence. Assuming that Vegard's law is valid for this ternary system, one can then calculate the perpendicular lattice parameter of the silicide and, hence, the expected 2θ value for (020) x-ray diffraction from such a relaxed layer. The calculated value for the case of $x=0.82$ (see Fig. 2) is $2\theta=58.589°\pm0.004°$. This exceeds the experimental value of $58.457°\pm0.006°$, indicating that the lattice is expanded in the direction perpendicular to the interface (positive elastic strain), hence it must be compressed biaxially parallel to the interface. A positive perpendicular strain is also what should be expected from the calculated lattice mismatches (Table I).

Since the elastic constants of $Re_xMo_{1-x}Si_2$ are unknown, we cannot calculate the expected perpendicular strain in the case of pseudomorphically grown layers. However, a large dechanneling peak observed at the silicide/substrate interface in all channeling spectra proves that crystalline defects exist in the layers near the interface. Since the films are compressively strained, these defects probably include misfit dislocations that partially relax the elastic strain of the films (see, for example, Fig. 3, showing an interface peak in the Re signal at an energy of about 2200 keV).

A perpendicular strain of $e^{\perp}=+0.48\%$ and $e^{\perp}=+0.21\%$ is found on the basis of Vegard's law for $x=0.68$ and $x=0.82$, respectively. Although it has a smaller lattice mismatch, the latter sample is more relaxed than the former. This fact is attributed to the much larger thickness of the Re-rich layer (2600 Å compared to only 1100 Å). The higher minimum yield found in the channeling experiments for $x=0.82$ compared to $x=0.68$ might be related to this enhanced relaxation.

IV. SUMMARY AND CONCLUSION

In summary, we find that ternary $Re_xMo_{1-x}Si_2$ can be formed with reactive deposition epitaxy. Whereas reactive deposition epitaxially-grown $MoSi_2$ is polycrystalline, these ternary silicides exhibit a good alignment with the Si(100) substrate, at least up to a Mo fraction of $\frac{1}{3}$. The next step will be to examine how the band gap varies with this composition.

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