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CHARACTERIZATION OF EPITAXIAL GROWTH OF SEMICONDUCTING RHENIUM "DISILICIDE" FILMS

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ABSTRACT

We have characterized, through transmission electron microscopy (TEM), the ReSi$_{2-x}$ thin
films grown by reactive deposition on (001) Si. ReSi$_{2-x}$ thin films exhibit a distorted body-
centered tetragonal MoSi$_2$-type structure, and have excellent epitaxy on (001) Si since the face
diagonal of the Si unit cell is equal to the c lattice parameter of silicide. The Si-deficient
composition in the "disilicide" may be accommodated by collapse and shear of missing Si planes
to form planar faults. Kirkendall voids are also observed at the film-substrate interface. The
engineering of the defect and interface structures of these complex, non-stoichiometric silicides
for optimized optoelectronic properties are discussed.

INTRODUCTION

ReSi$_2$ is usually reported to have the body-center
tetragonal (bct) C$_{11b}$ MoSi$_2$ structure shown in Fig. 1 [1].
However, unlike MoSi$_2$ which is metallic, ReSi$_2$ is a
semiconductor [1]. As shown in Table 1, a variety of different
structures, stoichiometries and band gap values have been
reported for this material [1-9]. Early work on band structure
calculations using the C$_{11b}$ structure and ReSi$_2$ stoichiometry
[10,11], predicted metallic behavior. Recently, Gottlieb
et al. [4] and our group [5,6] have shown that, for bulk crystals, the
stoichiometry is ReSi$_{1.75}$ and a range of monoclinic structures
derived from C$_{11b}$ structure are observed. First principles
calculations using the stoichiometry of ReSi$_{1.75}$ and the
monoclinic structure observed by Gottlieb et al. [4] have
indeed predicted a semiconducting behavior with an indirect
gap of 0.16 eV [12].

The narrow band gap of $\sim$0.15 eV offers the potential of developing ReSi$_{2-x}$-based long
wavelength infrared detection devices [13]. The potential of tuning the band gap by alloying with
Mo and epitaxial growth on Si [14] make this semiconducting silicide even more promising for
infrared detector applications. In particular, epitaxial ReSi$_{2-x}$ films on Si allow devices where the
detector element and the signal processing circuitry can be integrated on one Si chip, a feature
not possible in HgCdTe-based detectors [13]. A detailed characterization, using TEM, of the
microstructure of epitaxial ReSi$_{2-x}$ films on Si has not been performed. In this investigation, we
have characterized the epitaxial growth of ReSi$_{2-x}$ on Si to gain insight on the structure,
stoichiometry and the defect structures in the film and the interface.

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Table 1: Stoichiometry, structure and band gap values of bulk and thin film “ReSi$_2$”

<table>
<thead>
<tr>
<th>Composition</th>
<th>Structure type</th>
<th>Processing</th>
<th>Band Gap (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ReSi$_2$</td>
<td>Tetragonal C11$_b$</td>
<td>melting</td>
<td>0.12</td>
<td>1</td>
</tr>
<tr>
<td>ReSi$_{1.8}$</td>
<td>Tetragonal C11$_b$</td>
<td>melting</td>
<td>NR</td>
<td>2</td>
</tr>
<tr>
<td>ReSi$_{1.96}$</td>
<td>Orthorhombic distortion of C11$_b$</td>
<td>melting</td>
<td>0.2</td>
<td>3</td>
</tr>
<tr>
<td>ReSi$_{1.75}$</td>
<td>Monoclinic distortion of C11$_b$</td>
<td>Czochralski grown crystals</td>
<td>0.16</td>
<td>4</td>
</tr>
<tr>
<td>ReSi$_{1.75}$</td>
<td>Incommensurate or commensurate monoclinic structure based on C11$_b$</td>
<td>Float-zone or Czochralski grown crystals</td>
<td>NR</td>
<td>5,6</td>
</tr>
<tr>
<td>ReSi$_3$</td>
<td>Tetragonal C11$_b$</td>
<td>Polycrystalline films</td>
<td>0.12</td>
<td>7</td>
</tr>
<tr>
<td>ReSi$_3$</td>
<td>Tetragonal C11$_b$</td>
<td>Polycrystalline films</td>
<td>0.18</td>
<td>8</td>
</tr>
<tr>
<td>ReSi$_3$</td>
<td>Tetragonal C11$_b$</td>
<td>Epitaxial films</td>
<td>0.15</td>
<td>9</td>
</tr>
</tbody>
</table>

NR: not reported

EXPERIMENTAL PROCEDURES

ReSi$_{2.4}$ films were grown using the reactive deposition epitaxy (RDE) approach by depositing Re on (100) Si maintained at 650 °C in a UHV evaporator. A cap layer of Cr was evaporated at room temperature. Details of synthesis have been presented elsewhere [14]. Some films were synthesized by co-evaporating Re and Si (1:2 ratio) on (100) Si at room temperature followed by vacuum annealing at 850 °C for 30 minutes. Conventional TEM was performed on a Philips CM30 microscope and high resolution TEM was performed on a JEOL 3000F microscope, both at 300 kV. Rutherford backscattering spectroscopy (RBS) was performed using 2 MeV He+ ions.

RESULTS

A bright field (BF) TEM image of the RDE grown silicide film is shown in Fig. 2(a) along with the corresponding selected area diffraction pattern (SADP) in (b). The silicide diffraction spots are consistent with the bet MoSi$_2$ structure. No evidence of the incommensurate or commensurate monoclinic structures observed in bulk crystals [4-6] was found in these films. The orientation relationship was (001)Si // (010)silicide, [110]Si // [001]silicide and the SADP in Fig. 2(b) shows two variants of this relationship with [110]Si, [001]silicide and [100] silicide SADP superimposed. In Fig. 2(b), the [100] silicide pattern is marked with a rectangular box and indices underlined, the [001] silicide pattern with a square box and indices not underlined, and the [110] Si pattern with a dotted rectangular box and indices labeled as (hkl)Si. Good epitaxy is expected since the face diagonal of Si (a\sqrt{2}) is equal to the c lattice parameter of silicide. Note in Fig. 2(b) that the (220)Si and (004) silicide diffraction spots overlap. The microstructure of the film is columnar, with the columns being ~10-15 nm wide. In Fig. 2(a), it is indicated that the growth direction is [010] and the direction in the plane of the film could be [001] or [100] depending on the specific rotational variant of the column. RBS analysis indicated that the Si to Re atomic ratio in the silicide layer was ~1.8, close to the expected ReSi$_{1.75}$ stoichiometry.
In order to study these defects in detail, high resolution TEM was performed on an image, for the same orientation as in Fig. 2 but from a region with no interfacial voids, is shown in Fig. 3. Based on the information obtained from conventional TEM (Fig. 2), one would expect the high resolution TEM image to show about 10-15 nm wide regions viewed along the [001] or [100] axes of the unit cell shown in Fig. 1. In fact, some unit cells corresponding to the [100] and [001] orientations of the MoSi₂ structure are highlighted by rectangular and square boxes respectively in Fig. 3. However, the atomic resolution image shows no clear order in the plane of the film (horizontal direction in Fig. 3). To accommodate ReSi₂₃ stoichiometry in the MoSi₂ structure, there will be one missing Si plane every two unit cells.
These missing Si planes may manifest as stacking faults on (001). However, it is not obvious that the observed structure has an ordered arrangement of one missing Si plane every two unit cells. The faults may be more randomly arranged and may even be formed by two missing Si (001) planes in the C11\textsubscript{b} unit cell, as reported for MoSi\textsubscript{2} [15]. More detailed analysis, including image simulation, is needed to link the Si-deficient stoichiometry of the silicide and the corresponding atomic resolution images.

The ReSi\textsubscript{2-x}/Si interface exhibited voids at the interface on the Si side separated by good, void-free regions. One such void is shown in Fig. 2. We have also synthesized films by co-evaporating Re and Si on (100) Si at room temperature followed by high temperature vacuum anneals. The microstructure of these films along with the corresponding SADP is shown in Fig. 4. The void formation at the interface was significantly suppressed in these films (Fig. 4(a)). However, no clear epitaxy is noted and the diffraction pattern indicates a C11\textsubscript{b} structure with nanocrystalline grains.

**DISCUSSION**

The void formation at the interface and the epitaxial alignment of ReSi\textsubscript{2-x} films on (100) Si are discussed in this section.

The voids observed at the film/Si interface in RDE films may be explained as an effect of excess vacancy generation in the Si substrate due to silicide formation. Different mechanisms have been proposed for vacancy generation during the solid state metal-silicon reaction to form silicide: (i) Si diffuses more rapidly than metal (Kirkendall effect) [16], (ii) vacancies tend to relieve the build up of thermal stresses [17], and (iii) vacancies in Si account for volume contraction when silicide forms [18,19]. Recent studies by Herner \textit{et al.} [20] on TiSi\textsubscript{2} ruled out stress compensation and volume contraction as possible mechanisms. Itayantsev and Kuznetsov [19] have postulated that deformation mechanisms may be dominant only when metal diffusion is much more rapid than Si diffusion. For the case of Re-Si system, Si diffusion is far more rapid than Re and hence, diffusional mechanisms may be more relevant for interpretation of excess vacancy generation.

For metal-Si reactions to form silicides, an analysis of the marker motion to illustrate the Kirkendall effect was performed by Tu [21]. For ReSi\textsubscript{2-x} formation, Si diffuses out much more rapidly than Re diffuses in. Thus, for every Si atom from the substrate that crosses the interface
to form silicide, one vacancy will be left behind in the substrate. Evidence for this effect was provided by the following experiment of Wen et al [16] on the Ti-Si system: (i) interstitial defects were introduced in the Si wafer by ion irradiation, (ii) Ti was then deposited on the Si surface followed by high temperature anneal, (iii) as Ti silicide formed, the density of interstitial defects in Si was observed to decrease. The interpretation was that the vacancies introduced in Si as a result of silicide formation combined with the interstitials to reduce the interstitial defect density [16]. For the case of the Re-Si system, the concentration of the vacancies introduced following silicide formation may be estimated, to a first approximation, as being equal to the number of Si atoms/cm$^2$ in the silicide layer ($n_{Si}$) given by RBS. For the film shown in Fig 2, we estimated $n_{Si}$ as $\sim 4 \times 10^{17}$ atoms/cm$^2$. To a first approximation, this should also be the number density of vacancies introduced in Si. For Si with atomic density of $5 \times 10^{22}$ atoms/cm$^3$, if all the $4 \times 10^{17}$ /cm$^2$ vacancies collapse into voids, then the void thickness would be 80 nm with 100% interface coverage. The fact that experimentally we observed a void thickness of $\sim 20$ nm with less than 100% interface coverage of voids indicates that all the vacancies produced may not be collapsed into voids at the interface. Some vacancies may diffuse deeper into the substrate at the reaction temperature of 650 °C and/or combine with any pre-existing interstitials in Si. Further, the estimate of the number of vacancies produced is an upper bound since Re diffusion inwards along faults into Si is completely ignored. Nevertheless, this simple calculation shows that the concentration of excess vacancies injected into Si during ReSi$_2$$_x$ formation is significant and void formation at the interface is inevitable. The void thickness and the fraction of interface covered with voids may increase with increasing thickness of silicide layer formed by reaction of Re with Si substrate. Experiments to quantitatively correlate the film thickness and void content are in progress. If indeed the void formation is a result of Si from the substrate diffusing out to form the silicide, then co-deposition of Re and Si should suppress the void formation, as shown in Fig. 4. However, the results shown in Fig. 4 are preliminary since the surface of Si was not observed by reflection high energy electron diffraction prior to deposition (as was the case with RDE films). Any native oxide on Si not removed by HF etching may impede the outward diffusion of Si.

Excellent epitaxial alignment of ReSi$_2$$_x$ films on (100) Si inferred in earlier ion-channeling studies has been confirmed here by cross-section TEM. Though the films have columnar microstructure on the scale of 10-15 nm, all columns are well aligned and represent one or the other of the two rotational variants of the crystallographic orientation relationship. The fine-scale of the microstructure may be consistent with a nucleation-controlled formation of this silicide. In other words, the temperature is above the critical temperature that is need to form the “disilicide” but still low enough so that the silicide nuclei are very fine. Chu et al [22] have reported localized epitaxial growth of ReSi$_2$$_x$ on (100) Si by depositing Re at room temperature followed by a two-step 500-1100 °C annealing. The average grain size was reported to be 0.6 μm. Significant growth of the ReSi$_2$$_x$ nuclei was observed only above 1000 °C. However, no reports exist of epitaxial growth of ReSi$_2$$_x$ without voids at the interface. While co-deposition of Re and Si may suppress the reaction of Re with Si from substrate (and hence, the void formation), the films thus formed were not epitaxial. Using a Si to Re ratio of less than 2 and higher annealing temperature may promote solid phase epitaxy. Another approach to explore is using a very thin Re layer to form a seed layer of epitaxial silicide, followed by a co-deposited Re and Si layer to suppress consumption of Si from substrate; this may allow growth of epitaxial films with no interface voids. These experiments will be presented in a future article.
SUMMARY

Epitaxial growth of ReSi$_2$$_x$ with C11$_b$ MoSi$_2$ type structure has been observed using reactive deposition epitaxy. Incommensurate or commensurate monoclinic structures derived from the C11$_b$ structure that are observed in solidification-processed bulk crystals of this silicide were not found in thin films processed by solid state reactions. Films have columnar microstructure with grains exhibiting two variants of the orientation relationship: (001)Si // (010)silicide, [110]Si // [001]silicide. The Si-deficient stoichiometry in this “disilicide” may be accommodated by (001) stacking faults. Voids at the interface are interpreted in terms of the Kirkendall effect since Si diffuses much more rapidly in Re than vice-versa. Co-deposition of Re and Si seems to suppress void formation.

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REFERENCES