Final Report

NARROW BANDGAP SEMICONDUCTING SILICIDES:
INTRINSIC INFRARED DETECTORS ON A SILICON CHIP

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Abstract

Polycrystalline thin films of CrSi$_2$, LaSi$_2$, and ReSi$_2$ were grown on silicon substrates. Normal incidence optical transmittance and reflectance measurements were made as a function of wavelength. It was demonstrated that LaSi$_2$ is a metallic conductor, but that CrSi$_2$ and ReSi$_2$ are, in fact, narrow bandgap semiconductors. For CrSi$_2$, the complex index of refraction was determined by computer analysis of the optical data. From the imaginary part, the optical absorption coefficient was determined as a function of photon energy. It was shown that CrSi$_2$ possesses an indirect forbidden energy gap of slightly less than 0.31 eV, and yet it is a very strong absorber of light above the absorption edge. On the other hand, the ReSi$_2$ films exhibit an absorption edge in the vicinity of 0.2 eV. Measurements of the thermal activation energy of resistivity for ReSi$_2$ indicate a bandgap of 0.18 eV. It is concluded that the semiconducting silicides merit further investigation for development as new silicon-compatible infrared detector materials.
Introduction

In fulfillment of the technical objectives of our Phase I research contract, we have fabricated thin films of CrSi₂, LaSi₂, and ReSi₂, have characterized them structurally and compositionally, have measured the optical transmittance and reflectance, and have obtained optical constants from the data where the materials lend themselves to the techniques available to us. The details of this experimental work and analysis are presented in the following sections.

Experimental Procedure

Chromium, lanthanum, and rhenium films were deposited onto silicon substrates by neutralized ion beam sputtering from metal targets [1]. Substrates for optical properties measurements were 1-0-0 or 1-1-1 orientation, polished silicon wafers [2]. Metal films were also deposited onto similar wafers which were previously thermally oxidized and coated with undoped polycrystalline silicon (polysilicon) by low pressure chemical vapor deposition. (The polysilicon substrates were unsuitable for optical characterization; the purpose of these was to electrically isolate the silicide film from the silicon substrate to allow accurate resistivity measurements.) All substrates were ion milled within the vacuum chamber immediately prior to deposition, in order to obtain clean metal-silicon interfaces.

The silicide layers were formed by heating the samples in a quartz tube furnace under high purity flowing argon. In each case, the metal film was completely consumed by the substrate in forming the disilicide. The growth conditions were 120 minutes at 1100 for CrSi₂, 60 minutes at 600 or 900 C for
LaSi₂, and 60 minutes at 900 C for ReSi₂.

The lanthanum films were susceptible to a tarnishing reaction when exposed to air, such that over a period of a few hours a 5000 Å metal film would be converted entirely to lanthanum oxide. This was observed as a continual change in color of the film in reflection until the metal was totally oxidized. Auger analysis of a fully tarnished film showed a mixture of lanthanum and oxygen throughout the film thickness.

The tarnishing reaction was prevented by capping the lanthanum layer with about 300 Å of silicon prior to removing the sample from the ion beam deposition system. The silicon layer formed a thin SiO₂ native oxide which served as a diffusion barrier to the further incorporation of oxygen in the film. The silicon cap was also consumed during silicide formation.

The silicide thicknesses were obtained by measuring the metal thicknesses at a step created by masking during deposition. These thicknesses were calculated from density data neglecting strain and assuming bulk densities. Under such assumptions, the ratio of silicide to metal thicknesses is 3.01 for CrSi₂, 1.68 for LaSi₂, and 2.56 for ReSi₂ [3]. The thickest obtainable ReSi₂ film was ~800 Å, while in the cases of CrSi₂ and LaSi₂ films of more than a micron thicknesses were obtained with no indication of an upper limit. Rhenium films corresponding to silicide thickness greater than ~800 Å peeled off the substrates during annealing.

The normal incidence optical transmittance and reflectance were measured as functions of wavelength using a Perkin-Elmer 337 Grating Infrared Spectrophotometer for the wavelength range from 3 to 25 microns. For wavelengths shorter than 3 microns, an optical bench with infrared source, grating monochromator, order sorting filters, light chopper, and HgCdTe detector was used. The transmittance of a sample was normalized to that of a
bare half of the substrate. The reflectance was obtained with the aid of a Perkin-Elmer specular reflectance accessory.

The complex index of refraction of the film was extracted from the optical data with the aid of a two-layer optical model [4]. The model considered absorption in the silicide film and multiple reflections within both the silicide film and the substrate. Equations for the measured transmission and reflection were derived from the optical model. These depend on (1) the wavelength, (2) the index of refraction, extinction coefficient, and thickness of the silicide film, and (3) the index of refraction and thickness of the substrate. All other quantities being known, the optical constants of the silicide films were determined from these equations and the data.

The determination of the optical constants was a three-step process because of the transcendental nature of the equations, and because they contain periodic functions. First, all physically realistic pairs of the optical constants, which produce calculated transmittances and reflectances within five percent of the measured values, were determined with a grid search. These pairs of \( n \) and \( k \) were plotted as functions of wavelength. This produced several distinct continuous curves, corresponding to families of mathematically correct solutions [5]. The physically correct family was determined by comparing these solutions with an index of refraction value which was estimated from the interference fringes in the data. The final values of the optical constants were determined by refining this solution with a damped Newton-Raphson fit routine.

The optical characterization of the \( \text{ReSi}_2 \) thin films was not entirely possible with the techniques available to us because only very thin films could be obtained, as will be discussed below. Thus, to aid in the
interpretation of the optical data high temperature resistivity measurements were made with a vacuum system equipped with a tungsten wire four-point probe and heaters. The resistivity as a function of temperature was calculated from the measured sheet resistance and the film thickness. The intent was to obtain the thermal activation energy of conductivity within the intrinsic regime, which generally is equal to half the forbidden energy gap.

**Materials Characterization**

X-ray diffraction with copper Kα radiation was used for phase identification of the silicide films. It was found that a few prominent and unique peaks associated with each phase could be used.

A representative pattern for an hexagonal CrSi₂ sample is shown in Figure 1. The prominent peaks are labeled with their Miller indices [6] and are listed in Table I as well. In addition, the (003) peak at 42.6° was frequently observed. A so-called forbidden reflection from the single crystal silicon substrate appears at 32.9° alongside other reflections also due to the substrate.

There are two crystal structures for LaSi₂, a low temperature tetragonal phase, and a high temperature orthorhombic phase. The two annealing temperatures cited previously gave apparently single-phase films having each of these structures. Representative X-ray diffraction patterns are given in Figure 2. Unique and prominent peaks for each phase are listed in Table I [7]. Some strong reflections from the single crystal 1-0-0 silicon substrate are seen. Our conclusion that LaSi₂ is a metallic conductor is based on an examination of samples of both crystal structures.

Finally, a representative pattern for tetragonal ReSi₂ is shown in Figure 5.
Table I

Prominent X-ray Diffraction Peaks

<table>
<thead>
<tr>
<th>Material</th>
<th>Two Theta</th>
<th>Miller Indices</th>
</tr>
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<tbody>
<tr>
<td>CrSi₂</td>
<td>27.2°</td>
<td>101</td>
</tr>
<tr>
<td></td>
<td>40.7°</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>43.3°</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>47.5°</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>50.2°</td>
<td>112</td>
</tr>
<tr>
<td>LaSi₂</td>
<td>21.9°</td>
<td>101</td>
</tr>
<tr>
<td>Tetragonal (600C)</td>
<td>32.4°</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>42.4°</td>
<td>200</td>
</tr>
<tr>
<td>Orthorhombic (900C)</td>
<td>21.3°</td>
<td>010</td>
</tr>
<tr>
<td></td>
<td>28.4°</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>30.6°</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>31.9°</td>
<td>005</td>
</tr>
<tr>
<td></td>
<td>47.8°</td>
<td>210</td>
</tr>
<tr>
<td>ReSi₂</td>
<td>40.8°</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>45.8°</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>47.4°</td>
<td>112 and 004</td>
</tr>
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</table>

3. Unique and prominent X-ray diffraction peaks for this phase are also listed in Table I [8]. Reflections from the single crystal 1-1-1 silicon substrate are apparent.

In summary, for all three semiconducting silicides the X-ray diffraction data indicate that polycrystalline films of the desired compounds were
obtained, with no evidence of other silicide phases or unreacted metal.

Representative Auger spectra are shown for the three materials in Figures 4 - 6. The spectra were obtained after ion milling the samples in order to remove adsorbed impurities. It is found that the impurity levels within the interior of the films are at or below background levels for the instrument. Peaks for silicon and the respective metals are prominent.

SEM top views and fracture cross-sections are shown in Figures 7 - 9. These approximately confirm the thickness estimates from metal film thicknesses as discussed above. In all cases, there is a sharp interface between silicide film and silicon substrate. The top views show that surface roughness of the CrSi$_2$, while certainly observable, may be presumed to not greatly influence the optical properties since it is of a much smaller size range than the optical wavelengths of interest [9]. Microcracks were sometimes observed in the thickest CrSi$_2$ films, as shown in the left hand side of Figure 7(a). The LaSi$_2$ films are quite rough and of a nonuniform thickness but this is not an issue for optical characterization since the material is not a semiconductor. The ReSi$_2$ film thickness seems to be of sufficient uniformity for optical characterization.

**Optical Properties Measurements, Analysis, and Discussion**

The optical properties of four CrSi$_2$ films of four different thicknesses are shown in Figure 10. The onset of strong absorption depends on film thickness, moving to lower photon energy for thicker films. Interference fringes, due to multiple internal reflections within the silicide layer are also seen. The real part (n) of the complex index may be estimated from the positions of adjacent extrema in the reflectance spectra using the following equation [10]:

\[
n = \frac{r_{max} + r_{min}}{r_{max} - r_{min}}
\]
\[ n = \frac{\lambda_1 \lambda_2}{2d(\lambda_1 - \lambda_2)}. \]  

\( \lambda_1 \) and \( \lambda_2 \) are the wavelengths corresponding to adjacent reflectance minima and \( d \) is the film thickness. The value obtained for \( n \) is \(-7.5\).

The optical absorption coefficient \((\propto)\), calculated from

\[ \propto = \frac{4\pi}{\lambda} k, \]  

is shown in Figure 11. \( k \) is the imaginary part of the complex index. There is a very strong absorption edge in the vicinity of 0.3 eV which is due to interband transitions, with very high values of the absorption coefficient observed above the edge.

In addition, for photon energies below ~0.2 eV there is an increase in absorption coefficient with decreasing photon energy. The energy dependence here is like that expected for free carrier absorption, and the magnitude and energy range is consistent with that interpretation. An alternative explanation of the sub-bandgap absorption is diffuse scattering due to surface roughness. We are unsure which interpretation is correct; fortunately the phenomenon does not interfere with our determination of the value and type of forbidden energy gap in this material.

The absorption coefficient data are replotted in Figure 12 in a manner that would yield a linear plot for indirect transitions. Actually two linear regimes are predicted, with the two intercepts being the value of the forbidden energy gap \((E_g)\) plus or minus the energy of the phonon \((E_p)\) required for \(k\)-conservation [11]:

\[ \frac{\lambda_1 \lambda_2}{2d(\lambda_1 - \lambda_2)}. \]
\[ (\alpha)^{1/2} = C(h\nu - E_g + E_p). \]  

(3)

C is a constant depending on the details of the band structure, \( \nu \) is the photon frequency, and \( h \) is Planck's constant.

The excellent linear behavior of the data in Figure 12 suggests strongly that the gap is indirect. Only the phonon emission part of the curve is seen however, with an intercept of 0.31 eV. It is necessary, generally, to work with bulk samples if one is to observe the phonon absorption branch. For example, the absorption coefficient within the phonon absorption range is on the order of 10 cm\(^{-1}\) or lower for silicon and germanium. We conclude that the indirect gap of CrSi\(_2\) is slightly less than 0.31 eV by an amount equal to \( E_p \). This phonon energy is typically a few hundredths of an eV.

There may be direct transitions in CrSi\(_2\) at higher energies. Figure 13 shows the data for one sample plotted in a manner appropriate for direct transitions, with the scale chosen to display the behavior well above the fundamental edge. For direct transitions, we have [11]

\[ (\alpha)^2 = D(h\nu - E_d). \]  

(4)

\( D \) is another constant that depends on the band structure and \( E_d \) is the minimum direct gap. The value of \( E_d \) from Figure 13 appears to be on the order of 0.57 eV.

All of the LaSi\(_2\) films were found to be opaque. That is, there was no measurable transmittance at any wavelength accessible to us for even the thinnest films (\(~900\) A). This behavior is characteristic of the as-deposited metal films and of well-known metallically conducting silicides (TiSi\(_2\), MoSi\(_2\), TaSi\(_2\), and WSi\(_2\)) we have made in other research. From sheet resistance
measurements of LaSi$_2$ films formed on polysilicon substrates, we obtain room
temperature resistivities of 44 and 81 micro-ohm-cm for the tetragonal and
orthorhombic phases, respectively. The resistivity of representative samples
of the two LaSi$_2$ phases is shown as a function of temperature in Figure 14.
The linear behavior is typical of metallically conducting materials.

Some optical data for ReSi$_2$ are shown in Figure 15. There is an
absorption edge in the vicinity of 0.2 eV. We have obtained no clear energy
dependence of the optical absorption coefficient for this material, because
the previously mentioned difficulties with film fabrication prevented our
obtaining films with sufficiently strong absorption. To our knowledge, there
is no report in the scientific literature of the formation of ReSi$_2$ thin films
by any means [12].

Our problem specifically is that the computer is unable to find solutions
to the expressions for reflectance and transmittance for weakly absorbing
samples. There is no fundamental physical or computational reason for this,
but apparently there is such an interplay between n and k in the expressions
that a large number of combinations may be fitted with essentially the same
accuracy to a given experimental pair of reflectance and transmittance values.
Thus, it has not been possible to achieve the same level of analysis for ReSi$_2$
as for CrSi$_2$. Earlier this year we found the same problem with the optical
analysis of IrSi$_{1.75}$ thin films. (The iridium silicide could be grown only as
very thin films, and only on 1-l-1 wafers.)

The electrical resistivity of ReSi$_2$ is shown as a function of temperature
in Figure 16. The material apparently is in the intrinsic regime, with the
data exhibiting a thermal activation energy of ~0.09 eV. Above 670K (1000/T =
1.5), substrate shorting commences as the oxide becomes sufficiently
conductive and the apparent activation energy approaches that of intrinsic
silicon, 0.55 eV.

According to basic semiconductor band theory, the intrinsic resistivity activation energy should be half the bandgap \([13]\). Thus we estimate a forbidden energy gap of 0.18 eV for this material, which is in rough agreement with the optical data of Figure 15.

Our results on ReSi\(_2\) contradict a most recent theoretical investigation of the material in which a metallic band structure was predicted \([14]\). Using fully relativistic pseudopotentials, the energy bands, density of states, and Fermi surface were calculated. It was claimed that the conductivity of ReSi\(_2\) should be larger by far than that of MoSi\(_2\) or WSi\(_2\). On the other hand, the transparency and thermally activated resistivity we have observed show unequivocally that the material is a narrow bandgap semiconductor. Further research on ReSi\(_2\) film formation is needed in order to obtain samples adequate for detailed optical characterization such as was achieved for CrSi\(_2\).

**Summary and Conclusions: Phase II Research**

CrSi\(_2\) was found to possess an indirect forbidden energy gap of slightly less than 0.31 eV. Both forms of LaSi\(_2\) are metallic conductors and hence merit no further consideration as intrinsic semiconductor infrared detector materials. ReSi\(_2\) apparently has a gap of \(-0.18\) eV; difficulties with thin film formation prevented a detailed optical analysis of the material.

We find that CrSi\(_2\) and ReSi\(_2\) are interesting candidates for development as intrinsic infrared detector materials. Because these materials are grown directly on silicon substrates, they are particularly interesting for the development of fully integrated optical detectors. The fabrication of focal plane arrays of intrinsic semiconductor detectors made within films of CrSi\(_2\) or
ReSi₂ should be a straightforward extension of present techniques for making PtSi and Pd₂Si Schottky barrier detector arrays.

In other research we have optically characterized thin films of semiconducting MnSi₁.₇. This material, being quite similar to CrSi₂ optically, is a very strong absorber and possesses an indirect gap of slightly less than 0.54 eV. Thus, the absorption edge at ~2.3 microns makes it suitable for use with the window of atmospheric transparency at 2.0 – 2.6 microns and shorter wavelengths.

Phase II research should focus on improved materials preparation, and on the effects of defects on the transport and photoelectronic properties. Recent articles have described the epitaxial growth of the chromium [15] and manganese silicides [16], but the single-crystal regions of the films were of limited size.

The heart of a Phase II research program should be the exploration of epitaxial growth by molecular beam epitaxy. The effects of defects should be investigated with careful materials characterization coupled with mobility measurements (e.g. Hall effect) and lifetime measurements (e.g. photoconductivity). With this knowledge base it should be possible to move with confidence into the area of device development. This may include research on insulators, doping processes, contacts, and patterning of the materials. The research will pay enormous dividends if the semiconducting silicides make it possible to achieve, in a practical way, a new family of integrated infrared detectors on silicon.

Our Phase I research has shown that the semiconducting silicides as a class of materials merit further investigation for use in the integration of optical detectors with silicon-based microelectronics.
1. The targets were fabricated by Varian Specialty Metals, Grove City, OH, and of the following purity: Cr (99.85%), La (99.9%), Re (99.9%).

2. Obtained from Monsanto Co., Dallas, TX.


7. Tetragonal peak positions obtained from Ref. 6, Card 6-047; orthorhombic peak positions calculated from the crystal structure data in Ref. 3.

8. Calculated from the crystal structure data in Ref. 3.


12. We have heard over the "grapevine" that workers at AT&T Bell Labs have tried, and were unsuccessful, to fabricate ReSi2 thin films.


Figure Captions

1. X-ray diffraction pattern for a representative CrSi$_2$ film grown on a 1-0-0 silicon wafer.

2. X-ray diffraction pattern for tetragonal (a) and orthorhombic (b) LaSi$_2$ films grown on 1-0-0 silicon wafers.

3. X-ray diffraction pattern for a representative ReSi$_2$ film grown on a 1-1-1 silicon wafer.

4. Auger electron spectrum for a representative CrSi$_2$ thin film.

5. Auger electron spectrum for a representative LaSi$_2$ thin film.

6. Auger electron spectrum for a representative ReSi$_2$ thin film.

7. SEM top view (a) and fracture cross-section (b) for a CrSi$_2$ film.

8. SEM top view (a) and fracture cross-section (b) for a LaSi$_2$ film.

9. SEM top view (a) and fracture cross-section (b) for a ReSi$_2$ film.

10. Optical properties of four CrSi$_2$ samples.

11. Optical absorption coefficient of CrSi$_2$, obtained from the data of Figure 10. The four symbols correspond to the four samples of Figure 10.

12. Absorption coefficient data for CrSi$_2$ plotted in a manner appropriate for an indirect gap.

13. Absorption coefficient data for CrSi$_2$ that suggests the occurrence of direct transitions above the band edge.

14. Electrical resistivity as a function of temperature for tetragonal (a) and orthorhombic (b) LaSi$_2$.

15. Optical properties of three ReSi$_2$ films of the following thicknesses: • 768 Å, o 461 Å, and + 307 Å.

16. Electrical resistivity versus reciprocal temperature for ReSi$_2$; solid lines correspond to the activation energies shown.
DIFRACTED INTENSITY (a+b)
$dN(E)/dE$ (e/h.)

KINETIC ENERGY (eV)
SQUARE Root of ABSORPTION COEFFICIENT

ENERGY (eV)