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Electrical and optical characterization of semiconducting Ru_2Si_3 films and single crystals

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Recently, Ru_2Si_3 has been predicted to be a direct semiconductor with a band gap of ≈0.8 eV. Since the corresponding wavelength of this potential light emitter coincides with the absolute absorption minimum of glass fibers of 1.5 μm, considerable attention has been attracted. Measurements of the temperature dependence of the electrical resistivity of silicide films on insulating substrates were carried out in van der Pauw geometry. The results were explained by assuming carrier hopping over grain boundaries. The optical absorption coefficient was measured on thin films grown on various substrates, on self-sustaining films, where the substrate was partly removed and on a single crystal by photothermal deflection spectroscopy. A direct band gap at 0.84 eV was found. The absorption coefficient is very low up to ≈1.5 eV, likely due to a low density of states, and then strongly increases at higher energies. The experimental results qualitatively confirm the predictions of the band structure calculations. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1402965]

I. INTRODUCTION

Silicon based light emitters are key elements for the development of silicon based optoelectronics. In spite of the considerable effort of many research groups, an efficient silicon based light emitting diode (LED) is not available yet. LEDs in the near-infrared, particularly at 1.5 μm, are technologically important as this wavelength corresponds to the absolute absorption minimum in glass fibers. Increasing interest has been devoted to β-$FeSi_2$ as a potential candidate for future silicon based LEDs. In this work another related compound was investigated: ruthenium silicide (Ru_2Si_3). *Ab initio* band structure calculations performed independently by two different groups[1,2] predicted a direct band gap around 0.45 eV for Ru_2Si_3. Regarding the calculations, it should be noted that the nature of the transition can be calculated with a high certainty, while generally the predicted width is too small by a factor of 2. Moreover, a large oscillator strength is expected for this direct transition, since the valence band maximum at the Γ point is predominantly of Si p character and the conduction band minimum is predominantly of Ru d character. This should allow direct dipole transitions with $\Delta 1 = 1$ across the direct gap, resulting in a large across-gap oscillator strength. High temperature resistivity measurements of arc-melted samples yielded band gaps between 0.7 and 1.2 eV.[3–5] Therefore, light emission is expected in the near-infrared. These unique properties make Ru_2Si_3 a promising silicon based material for light emission. Here, we present systematic studies of electrical resistivity measurements and optical absorption measurements on Ru_2Si_3 films on Si.

II. EXPERIMENT

Epitaxial Ru_2Si_3 films were grown on low doped Si(111) and Si(001) wafers ($p \geqslant 1800\ \Omega\,\text{cm}$) by molecular beam epitaxy. Details about the growth process and film morphology can be found in Refs. 6 and 7. Because the resistivity even of low doped substrates exceeds that of the film at temperatures above ≈600 K, polycrystalline films were grown on insulating substrates, like quartz or sapphire for the high temperature measurements. Attempts to grow epitaxial films on silicon on insulator or silicon on sapphire (SOS) substrates were not satisfying. The crystalline quality of those films was very poor compared to films on single crystalline silicon, most likely due to the relatively poor quality of the Si cap layer and the very different thermal expansion coefficient of the film and the substrate.

Four-point measurements of the electrical resistivity in van der Pauw geometry were carried out in a quartz tube in argon atmosphere at temperatures between room temperature and 900 K. The temperature was measured by a thermocouple situated directly below the sample. Needles made of a special high-temperature alloy (Duratherm) positioned in the four edges of the sample were used as electrical contacts. Without any additional metallization, the contacts showed ohmic behavior, a necessary precondition for the van der Pauw method. However, in order to achieve a lower contact resistance, several different metallizations were tested. Ohmic contacts were obtained by the use of aluminum, platinum, and gold. However, the contact resistance could not be lowered. Chromium and titanium are unsuitable; they both lead to a non-ohmic behavior. Therefore, the following measurements were performed without any additional metallization. A possible in diffusion of the metallization at high temperatures can be excluded.

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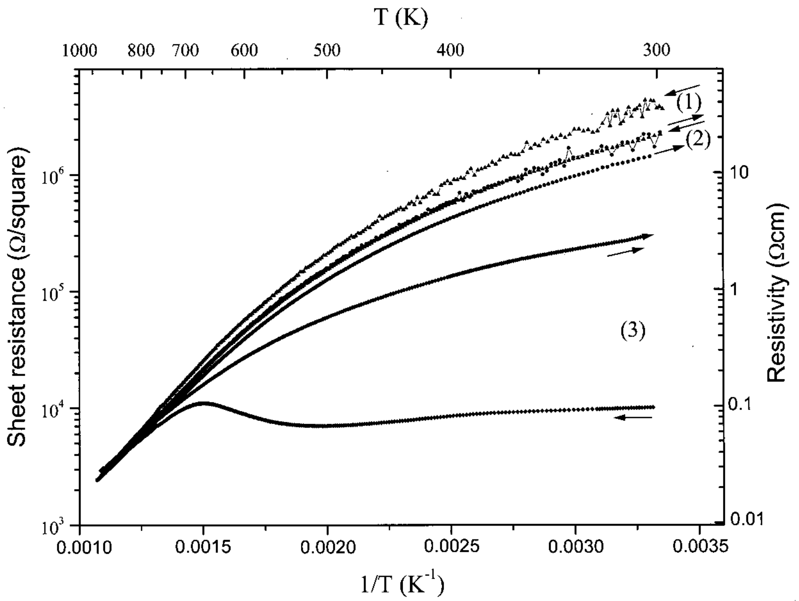

FIG. 1. Temperature dependence of the electrical resistivity of a 100 nm thick Ru_2Si_3 film on sapphire. The sample was heated to 900 K and cooled down to room temperature three times. Measurement (1) was carried out after an annealing at 1100 °C for 100 s, measurement (2) was repeated under the same conditions, measurement (3) was performed after an additional HF dip (10 s) (3). The arrows indicate the measuring direction.

Optical absorption was measured by photothermal deflection spectroscopy (PDS).[8] Light with varying wavelength is absorbed in the sample situated in a glass tube filled with a transparent medium, CCl_4. The absorbed light heats up the sample and leads to a temperature gradient above the sample. The resulting refractive index gradient causes deflection of a laser beam incident under a grazing angle. It can be shown that the deviation of the laser beam is proportional to the absorption in the sample. Because of its high sensitivity, temperature differences as small as 10^{-6} K can be measured. PDS has become a standard technique for measuring small absorption coefficients.

III. ELECTRICAL MEASUREMENTS

A. Results

Figure 1 shows the temperature dependence of the electrical resistivity of a 100 nm thick Ru_2Si_3 film on sapphire grown at a temperature of 800 °C and postannealed at 1100 °C for 100 s. A strong dependence on the pretreatment was found. Measurement (1) shows the resistivity during heating up and cooling down (indicated by the arrows). The relatively strong fluctuations at the beginning are caused by contact problems. They were observed in all samples but usually disappeared above 350 K. While cooling down, the resistivity does not exactly follow the curve during the heating up. It is assumed that during the measurement at high temperatures, contaminants present in the gas diffuse into the sample and change the carrier concentration slightly. This assumption is supported by the fact that the following measurement (2) exactly follows the cooling-down curve of measurement (1) and leads to further decreased resistivity values during the cooling-down cycle.

Measurement (3) was recorded after an additional HF dip for 10 s. This step is routinely done to remove oxide films eventually present on the surface after the rapid thermal annealing. The effect on the electrical resistivity is striking: The resistance decreased by 2 orders of magnitude and remained almost constant up to temperatures around 650 K. Then, the resistivity increases and qualitatively follows the behavior of the samples without HF treatment. Also during cooling down, the resistivity behaves similarly to the other two measurements; the effect caused by the HF seems to have disappeared. This process can be repeated many times. Alternating HF dips and annealings (above 700 K) allows us to switch between two "states" with low resistivity (after the HF dip) and high resistivity (after the annealing step).

B. Simulation

Before proposing a possible explanation of this effect, the first two measurements (1) and (2) will be discussed. At high temperatures, the resistivity ρ behaves as expected for a classical semiconductor, and it drops exponentially with increasing temperature. According to text books (e.g., Ref. 9), one obtains

$$\rho \propto \exp(E_G/2k_BT). \qquad (1)$$

This follows from $\rho=(en\mu)^{-1}$ for intrinsic semiconductors with parabolic bands, where the carrier concentration n is

$$n \propto T^{3/2} \cdot \exp(-E_G/2k_BT) \qquad (2)$$

and for a mobility μ limited by acoustic phonon scattering

$$\mu \propto T^{-3/2}. \qquad (3)$$

Fitting a straight line at high temperatures and using Eq. (1) to estimate the band gap leads to an unsatisfying large uncertainty of the band gap, varying between 0.7 and 1.0 eV, depending on pretreatment. Moreover, the exponentially decreasing resistivity already around room temperature cannot be explained by this simple model. Both problems can be eliminated by assuming an exponentially decreasing mobility, as explained in the following: In polycrystalline films a lot of dangling bonds are present at the grain boundaries. These interband states are able to capture free charge carriers. As a consequence, the grain boundaries charge up and the remaining charge carriers in the grains have to overcome these potential barriers to get from one grain to the other. According to a theory developed by Seto[10] and extended by Baccarani *et al.*,[11] one can distinguish two cases:

(1) All carriers are trapped at the grain boundaries and the grains are completely depleted in cases where the carrier concentration is low and/or the trap density is high. A current flow is only possible if the carriers are thermally activated into the conduction band. Assuming that the interband states are near the middle of the gap leads to an activation energy E_a around $E_G/2$.

(2) If the grains are only partially depleted, the activation energy E_a corresponds to the potential barrier E_B caused by the trapped carriers (at least if $E_B < E_G/2$). The potential barrier is given by

$$E_B = \frac{e^2 N_t^2}{8\varepsilon_0 N_D}, \tag{4}$$

where N_t and N_D are the trap density and the donor or acceptor concentration, respectively.

One obtains in both cases

$$\mu \propto \frac{1}{T}\exp\left(\frac{-E_a}{k_B T}\right). \tag{5}$$

The overall temperature dependence of the electrical resistivity is as follows: The temperature dependence of the carrier concentration consists of a temperature independent term resulting from the doping and a contribution from thermally activated carriers:

$$n(T) = N_D + N_0 T^{3/2} \cdot \exp(-E_G/2k_B T). \tag{6}$$

In the case of hopping over grain boundaries and considering acoustic phonon scattering, the temperature dependence of the mobility is

$$\mu(T) = \mu_0 T^{-3/2} \frac{1}{T}\exp\left(\frac{-E_a}{k_B T}\right). \tag{7}$$

This $T^{-3/2}$ dependence originating from the phonon scattering has already been observed by Gottlieb *et al.*[12] in single crystal Ru_2Si_3. Because the carrier concentration is the sum of two terms, it is easier to consider the conductivity σ instead of the resistivity. To obtain a reasonable least-square fit, it is favorable to use $\ln(\sigma)$ instead of σ as the fitting function, because σ is governed by its values at high temperatures and the agreement at low temperatures is very poor. So, the following fitting function was used (with $x = 1/T$):

$$\ln(\sigma) = \ln(x^{5/2}\exp(-a - bx) + x\exp(-c - dx)) \tag{8}$$

with

$$E_G = 2(d-b)k_B$$

and

$$E_a = bk_B. \tag{9}$$

Figure 2 shows the results of the least-square fit and Table I summarizes the resulting activation energies. It can be seen that by assuming an activated mobility caused by grain boundary hopping the measurements can be fully explained and consistent band gap values are found. The different slopes at high temperatures can be explained by different activation energies of the mobility. A comparison with other samples grown under different conditions leads to a band gap energy of 0.90±0.04 eV and a potential barrier between 0.13 and 0.18 eV.

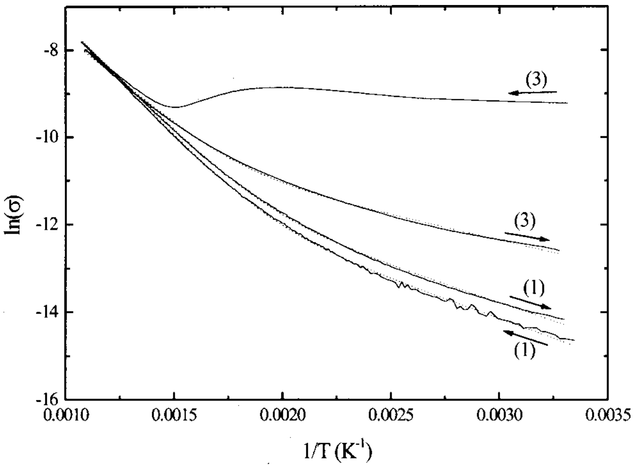

FIG. 2. Comparison of the measured and the simulated conductivity. The values determined are summarized in Table I. For better clarity, measurement (2) was omitted.

C. Effect of the HF etch

As shown in the previous figures, etching of Ru_2Si_3 in HF reduces the electrical resistivity by several orders of magnitude. The effect seems to be correlated with the passivation of dangling bonds at the grain boundaries. The hydrogen present in the HF solution diffuses along the grain boundaries into the silicide and passivates the dangling bonds. This is supported by two observations.

(1) The etch effect of polycrystalline and epitaxial (annealed and unannealed) films is compared in Fig. 3. The number of grain boundaries, and thus the number of dangling bonds, decreases from the polycrystalline samples to the epitaxial films to the epitaxially grown and annealed samples.[6] This corresponds to the resistivity change caused by the HF etching, which is by far the strongest in polycrystalline films, smaller in the epitaxial ones, and smallest in epitaxial annealed samples. The effect seems to be correlated with the number of dangling bonds.

(2) A further conclusive observation is that the effect disappears reproducibly by annealing the samples at temperatures above 650–700 K. It is known from other materials

TABLE I. Band gap energy E_G and potential barrier E_a for Ru_2Si_3 determined by Eq. (8).

Measurement	E_G/eV	E_a/eV
(1)↑	0.89	0.18
(1)↓	0.87	0.17
(2)↑	0.89	0.18
(2)↓	0.87	0.17
(3)↓	0.88	0.13

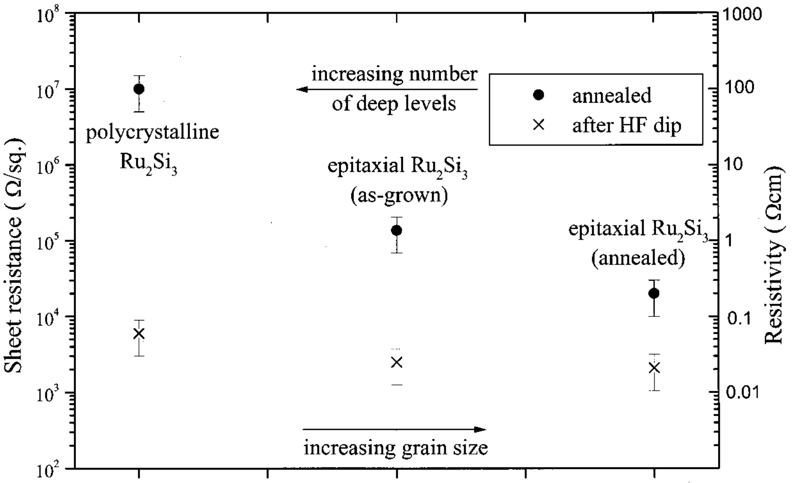

FIG. 3. Comparison of the HF dip effect on different substrates: Typical values of the electrical resistivity at room temperature of polycrystalline films, epitaxial, unannealed films, and epitaxial, annealed films are given.

that the effect of hydrogen passivation disappears by annealing around this temperature where the chemical bonds of the hydrogen to the defects break up.[13]

The behavior of the electrical resistivity can be consistently explained by hydrogen passivation of the dangling bonds. After the HF dip, the resistivity is much smaller because the dangling bonds are passivated and no potential barriers exist. As a consequence, the resistivity remains more or less constant (in other words $E_a=0$) up to 650 K, where the hydrogen bonds break up and the dangling bonds trap the carriers again. Potential barriers form and the resistivity increases up to values of samples without HF treatment. The HF effect has disappeared and the samples now behave like the ones without HF treatment.

IV. OPTICAL INVESTIGATIONS

A. Ru_2Si_3 on transparent substrates

Figure 4 shows a typical result of a PDS measurement of a 100 nm thick Ru_2Si_3 film on silicon. At low energies, the absorption is low, i.e., the film and the substrate are almost transparent [inset (1) in Fig. 4]. Around 1.1 eV the band-to-band absorption of Si sets in. The oscillations at higher energies arise from interferences of the reflected beam. This can be explained as follows: The absorption between 1.1 and 1.7 eV is too small to absorb the whole light in the 100 nm thick silicide film. Thus, a certain part of the light is reflected at the interface between silicide and silicon and interferes with the light reflected at the surface. This leads to oscillations in the reflected beam and causes the oscillations observed in the absorption spectrum (2). At energies above 1.8 eV the absorption in the silicide film is large enough to absorb the light completely, i.e., the penetration depth is less than 100 nm, and the oscillations vanish (3).

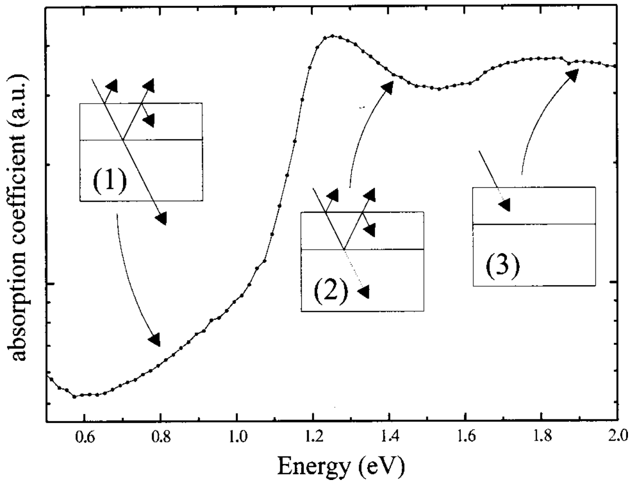

FIG. 4. Optical absorption of a 100 nm thick Ru_2Si_3 film on silicon: (1) Both Ru_2Si_3 and Si are transparent, (2) Si absorbs the light, interferences occur in the reflected beam, (3) the light is completely absorbed in the Ru_2Si_3.

At first sight, this result is surprising and not in agreement with the band gap of 0.9 eV determined by the electrical measurements. There is no absorption edge visible at this energy. From the spectrum, it can only be concluded that the absorption above ≈1.8 eV is sufficiently large to absorb the light within a 100 nm thick film. The Ru_2Si_3 absorption at lower energies cannot be determined accurately because the interesting range is distorted by the Si absorption edge. For this reason, polycrystalline films were prepared on various transparent substrates, like glass, sapphire, and SOS.

Figure 5 shows the absorption measurements for a Ru_2Si_3 film on a SOS substrate. As expected, the absorption is very low at low energies. Above 1.5 eV the absorption coefficient rises considerably. These results are in very good agreement with ellipsometry data by Henrion *et al.*[14] on polycrystalline films on Si. The low absorption coefficient complicates the determination of the band gap energy and, in addition, the interferences originating from the three layer system (Ru_2Si_3/Si/sapphire) hinder a quantitative evaluation. As a consequence, two layer systems, i.e., without intermediate Si film, were grown. A simulation of the interference effects should be much easier in this case, but another problem arises. The measured absorption coefficient at low energies is much larger compared to films grown on an intermediate Si film (not shown). We assume that in the present case the film has a composition different from the stoichiometric value and consists of two phases, the line compound Ru_2Si_3

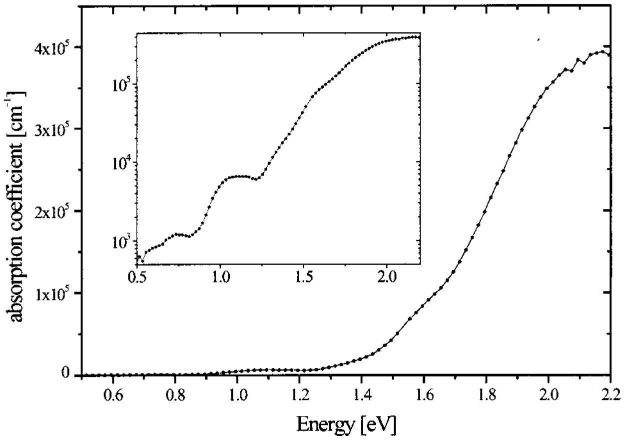

FIG. 5. Absorption coefficient of a 140 nm thick Ru_2Si_3 film on SOS. The inset shows the same curve on a logarithmic scale.

and, presumably, excess Ru. In the following, we describe an alternative approach.

B. Self-sustaining Ru_2Si_3 films

Epitaxial films were grown on Si, annealed at 1100 °C for 100 s and subsequently a window was etched in the back of the substrate to remove the silicon completely in this area. This allows us to measure the absorption coefficient of the silicide film through the hole directly without disturbing effects of the substrate.

To fabricate a self-sustaining Ru_2Si_3 film the samples were covered with 500 nm Si_3N_4 on both sides. A window was opened in the Si_3N_4 film on the back by standard optical lithography and reactive ion etching. The transfer of the pattern into the substrate was done by ething in hot KOH for several hours. The etching stops at the silicon–silicide interface. We produced self-sustaining 100 nm thick Ru_2Si_3 films with window sizes up to 4×2 mm^2. Unfortunately, the resulting absorption coefficient (Fig. 6) does not behave as expected. The absorption at low energies appears even larger than in films grown on transparent substrates (without intermediate Si film). A determination of the band gap is again not possible. So far this phenomenon, probably an artifact caused by the sample preparation, could not be explained.

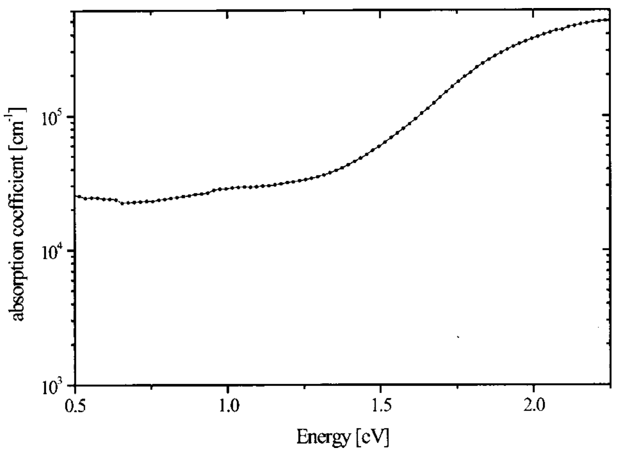

FIG. 6. Absorption coefficient of a 100 nm thick self-sustaining Ru_2Si_3 film. At low energies, it is much larger than the films on SOS substrates (compare Fig. 5).

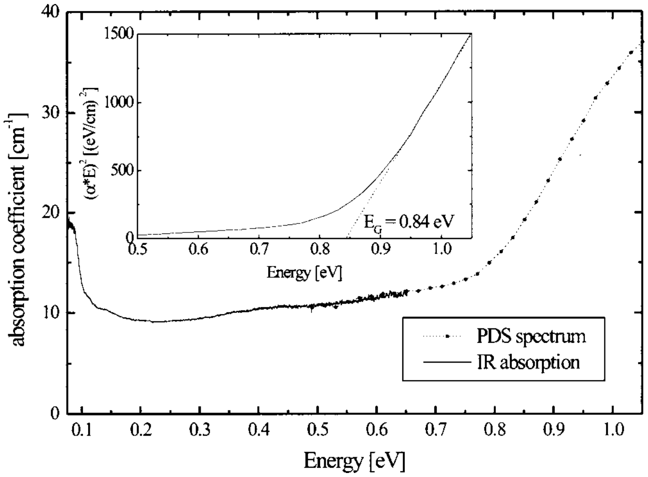

FIG. 7. Absorption coefficient of a Ru_2Si_3 single crystal. In addition to the PDS spectra, the IR absorption was measured. The increased absorption below 0.1 eV is caused by free carrier absorption. The inset shows the typical $((E-E_G)/E)^{1/2}$ dependence characteristic of a direct semiconductor.

C. Ru_2Si_3 single crystals

In order to investigate the range of low absorption near the band gap, the absorption coefficient of a single crystal was measured. The result is shown in Fig. 7. The much larger thickness (457 μm) allows the measurement of the very small absorption coefficient but has the disadvantage that an absorption coefficient far below 100 cm^{-1} is already sufficient to reach total absorption. Therefore, the measurement is limited to energies below ≈1 eV.

Figure 7 clearly shows an absorption edge around 0.8 eV. The inset shows the typical $(E-E_G)^{1/2}/E$ dependence characteristic for a direct transition. From the extrapolation one obtains a band gap value of 0.84 eV in agreement with measurements performed by Henrion *et al.*[15] The increased absorption below 0.1 eV is caused by free carriers. Using the relationship

$$\omega_p^2=\frac{ne^2}{m_e^*\varepsilon_0} \tag{10}$$

yields for a free electron gas ($m_e^*=m_e$) a background doping level of approximately 7×10^{18} cm^{-3}. A comparison of Figs. 5, 6, and 7 reveals that the absorption coefficient in the single crystal is much smaller than in the films. All films showed absorption coefficients larger than several 100 cm^{-1}. An additional effect much cause large absorption in the films which hides the band-to-band absorption of Ru_2Si_3. At present we can only speculate about the reason. A fundamental difference between the films and the single crystal are the grain boundaries, which may be responsible for the larger absorption of the films.

D. Luminescence

At 4 K, neither the films nor the single crystal showed photoluminescence between 0.4 and 1.3 eV. It is assumed that the luminescence is quenched by the deep levels at the grain boundaries and probably by impurities.

V. CONCLUSIONS

Measurements of the optical absorption yielded a direct band gap of 0.84 eV in good agreement with the value of 0.9 ± 0.04 eV determined from the temperature dependent resistivity measurements. At low energies the absorption coefficient is rather small, but strongly increases above 1.5 eV. How does this compare with the band structure calculations predicting a band gap of 0.42 eV? As already mentioned, the true band gap can be a factor of 2 larger than the theoretically predicted one. The increase of the absorption at 1.5 eV can be explained by an increase of the density of states. The band structure calculations yielded a very low density of states within the first 0.5 eV of the valence band (below the band gap).[1,2] Thus, the combined density of states is small between 0.9 eV and approximately $0.9 + 0.5$ eV, resulting in a small absorption coefficient below ≈ 1.4 eV.

The absorption coefficient at the band edge is several orders of magnitude smaller than, e.g., in GaAs. It cannot be concluded whether this is caused only by a low density of states or in addition, by a low oscillator strength. Anyway, both are not favorable for light emission because the radiative recombination rate is, like the absorption coefficient, basically determined by the product of combined density of states and oscillator strength. Efficient light emission is expected only if the nonradiative recombination rate is much smaller than the (already small) radiative recombination rate. Therefore, extremely pure and defect free material is a necessary precondition for using Ru_2Si_3 as a light emitter. Both conditions are difficult to fulfill:

(1) Ru is available only with a limited purity of 99.99%. Most of these contaminations have a larger vapor pressure than Ru, yielding to an even larger amount of impurities in the sample than originally present in the source material. At the moment, the use of evaporation methods, like MBE, seems to be critical.

(2) Because of the different rotational symmetries of silicon and Ru_2Si_3, the growth of single crystal (untextured) films seems very difficult. However, a considerable reduction of nonradiative recombination paths would be possible if one succeeds in growing larger grains. Therefore, further growth studies are necessary.

VI. SUMMARY

Temperature dependent measurements of the electrical resistivity of polycrystalline Ru_2Si_3 films on insulating substrates were presented. Assuming that the charge transport proceeds via hopping over grain boundaries the experimental data can be fully explained, resulting in a band gap energy of 0.9 ± 0.04 eV. The dangling bonds at the grain boundaries can be passivated by hydrogen diffusing into the sample in a HF solution. After the HF dip the resistivity is smaller by 2 orders of magnitude than before. The effect disappears by annealing the sample above ≈ 700 K because the bonds from the hydrogen to the defects break up at these temperatures.

The measurements of the optical absorption of films and of a single crystal yielded a direct band gap at 0.84 eV. The absorption is very low up to energies around 1.5 eV. At higher energies, the absorption coefficient rises considerably. This can be understood in terms of the predicted band structure. Because of the strong *p* character of the valence band, the density of states is low, up to approximately 0.5 eV below the band edge. Therefore, the combined density of states is low between 0.9 and ≈ 1.4 eV, as reflected in the absorption coefficient.

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