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The resistivity and Hall coefficient of CoGe and $CoGe_2$ thin films

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Abstract. This is a report of measurements of the electrical resistivity and of the Hall coefficient of CoGe and $CoGe_2$ films between 80 and 520 K. Both germanides behave as metallic conductors with resistivities increasing linearly with increasing T over the whole temperature range. There is a slight deviation from linearity for $CoGe_2$ which is attributed to the fact that the mean free path of the carriers becomes comparable with the lattice dimensions at high temperatures. The Hall coefficient is negative for CoGe, giving an apparent carrier concentration of $(0.86 \pm 0.01) \times 10^{28}\ \mathrm{m}^{-3}$ and a Hall mobility of $(11.0 \pm 0.1) \times 10^{-4}\ \mathrm{m}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$ at room temperature. On the other hand, p-type conduction is revealed for $CoGe_2$ with apparent carrier concentration and Hall mobility equal to $(1.93 \pm 0.01) \times 10^{28}\ \mathrm{m}^{-3}$ and $(2.2 \pm 0.1) \times 10^{-4}\ \mathrm{m}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$, respectively, at 300 K. For a quantitative explanation of the resistivity and Hall behaviour of germanides, detailed information about the energy band structure near the Fermi level is required. As this information is lacking, the rough approximation of the two-band model is the only way to obtain insight into the electrical properties of germanides.

1. Introduction

In the last few years, metal silicides have been used as Schottky barriers and ohmic contacts in microelectronics (Tu and Mayer 1978). This prompted the study of the kinetics of formation, the structure and in particular the electrical conduction behaviour of these materials, which can range from metallic to semiconducting (d'Heurle *et al* 1980, 1986, Murarka 1983, Malhotra *et al* 1984, Woerlee *et al* 1984, Krontiras *et al* 1987, 1988). Recently, attention has been focused on the analogous materials, germanides, which are suitable for use in infrared detectors and they give the possibility of studying the formation and properties of compounds resulting from the same metals as silicides but with a different semiconductor element, namely Ge (Majni *et al* 1977, Ottaviani *et al* 1977, Marshall *et al* 1985). The construction and characterisation of CoGe and $CoGe_2$ thin films and the measurement of their resistivity and Hall coefficient as functions of temperature presented in this paper is a small contribution to the effort to study the electrical properties of germanides.

Experimental and theoretical energy band studies of silicides have revealed a very complicated structure of the bands near the Fermi level (Weaver *et al* 1981, Martinage

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1989, Söldner *et al* 1989). This complexity makes it impossible to explain the resistivity and Hall effect of silicides on the basis of the quantum mechanical model, in which these properties depend on the mean free path of the carriers, the area and the curvature of the Fermi surface (Ziman 1972). Instead, the two-band model for degenerate isotropic materials is generally applied for a simplified interpretation of the transport properties of silicides. Although for the analogous compounds, germanides, energy band data are lacking, an electronic structure of similar complexity is expected, making the two-band model the only applicable method for germanides as well.

In the following, the sample preparation and the structural and compositional characterisation of the films are described and the resistivity and Hall coefficient experimental results are presented and discussed.

2. Experimental procedure

The samples were prepared by evaporating a thin film of Ge (4000 Å) and then, without breaking the vacuum, another of Co (700 Å) onto oxidised silicon wafers. Subsequently, the Co film was covered by a thin layer of Ge (150 Å) to avoid oxidation of the metal. The oxidised silicon wafers were cleaned by organic solvents and then were loaded into an oil-free electron gun evaporation system. The depositions of Ge and Co were carried out at pressures of less than 10^{-6} Torr. The germanide samples were subsequently prepared by annealing in a quartz tube vacuum furnace at 8×10^{-7} Torr. Two series of CoGe thin films were prepared by annealing for 30 min at two different temperatures: 400 and 450 °C. The $CoGe_2$ samples were prepared by a two-step procedure. First the monogermanide CoGe was formed by annealing for 30 min at a relatively low temperature (450 °C) and then the digermanide $CoGe_2$ was formed by increasing the temperature, without breaking the vacuum, to 650 or 750 °C for a further 30 min.

The thickness and composition of the resulting germanide thin films were determined by 2 MeV $^4He^+$ Rutherford back-scattering spectroscopy. The crystallographic phases were identified by x-ray diffraction analysis.

The electrical resistivity and Hall effect measurements were carried out on 6 mm × 6 mm square specimens attached to a sample holder in a cryostat, in which the temperature was stabilised to ±0.1 K at any value between 80 and 530 K. A magnetic field of 1.5 T from a conventional electromagnet was used for Hall effect measurements. To determine the resistivity and Hall coefficient the DC van der Pauw method was employed, in which four electrical contacts were made by pressing tungsten wire probes against the corners of the sample. A current of a few milliamperes was used in all measurements to avoid heating the samples. The power consumed on the sample was always less than 1 mW.

The linearity of the Hall voltage versus current or magnetic field was confirmed for all measured samples.

3. Results and discussion

As the 2 MeV $^4He^+$ Rutherford back-scattering spectroscopy indicated, cobalt had fully reacted with the underlying germanium layer and formed $CoGe_{1.0\pm0.1}$ (thickness, 1700 ± 100 Å) and $CoGe_{2.0\pm0.1}$ (thickness, 3100 ± 100 Å) at 400 or 450 °C and 650 or 750 °C, respectively. Moreover, the x-ray diffraction patterns of the samples included

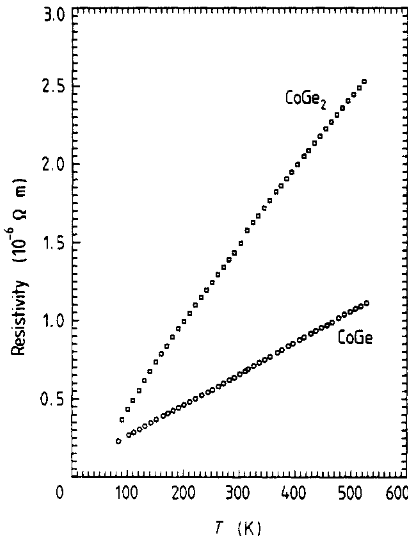

Figure 1. Electrical resistivity as a function of temperature for CoGe and $CoGe_2$ films.

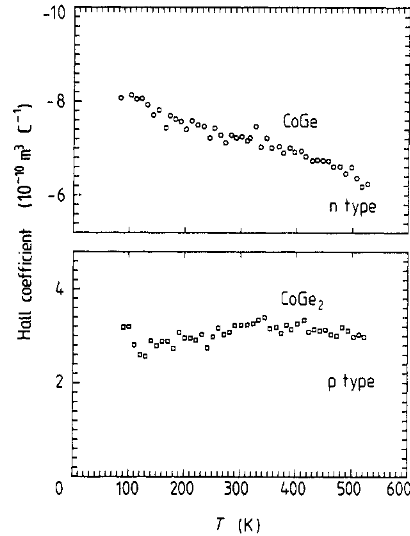

Figure 2. Hall coefficient as a function of temperature for CoGe and $CoGe_2$ films.

all the prominent CoGe and $CoGe_2$ powder peaks given in the ASTM files. From these patterns it was deduced that CoGe is monoclinic and $CoGe_2$ orthorhombic.

The samples of CoGe annealed at 400 °C gave the same resistivity and Hall effect curves as those annealed at 450 °C. The same was shown by the $CoGe_2$ samples annealed at the two different temperatures; so, in the following, we shall give the experimental results for CoGe and $CoGe_2$ films annealed at 400 °C and 750 °C, respectively.

The resistivity versus temperature curves for CoGe and $CoGe_2$ films are shown in figure 1. The fitting of these data using Matthiessen's rule and the Bloch–Grüneisen formula (Krontiras *et al* 1987) gives the values $\rho_0 = (15 \pm 2) \times 10^{-8}\ \Omega$ m, $\Theta = 400 \pm 10$ K, $\rho_\Theta = (90 \pm 2) \times 10^{-8}\ \Omega$ m for CoGe and $\rho_0 = (15 \pm 2) \times 10^{-8}\ \Omega$ m, $\Theta = 230 \pm 20$ K, $\rho_\Theta = (150 \pm 5) \times 10^{-8}\ \Omega$ m for $CoGe_2$, where ρ_0 is the residual resistivity, Θ is the Debye temperature and ρ_Θ is the temperature-dependent resistivity component at $T = \Theta$. The value of ρ_0 is only a rough approximation, as there are no experimental points for temperatures less than 80 K. In figure 2 the Hall coefficient is shown as a function of temperature; in figures 3 and 4 the apparent carrier concentrations deduced from equation $n = 1/e|R_H|$ and in figure 5 the Hall mobilities $\mu_H = |R_H|/\rho$ versus temperature are presented for the two germanides.

If we assume two carriers per unit cell in CoGe and three in $CoGe_2$, we get the carrier concentrations $n = 0.93 \times 10^{28}\ m^{-3}$ for the former and $0.86 \times 10^{28}\ m^{-3}$ for the latter. From the free-electron model and the relaxation time approximation, the following simple expression for the mean free path l of the carriers can be derived:

$$l = (\hbar/\rho e^2)(3\pi/n^2)^{1/3}.$$

This equation, by substitution of the experimental values of ρ at room temperature and the calculated values of n for two and three carriers per 'molecule' in CoGe and $CoGe_2$, respectively, gives l values of 20 Å for the former and 10 Å for the latter. We see that the mean free paths are two orders of magnitude lower than the thicknesses of the films.

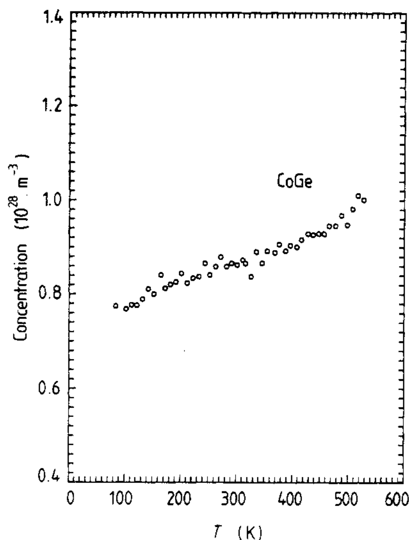

Figure 3. Carrier concentration deduced from the Hall coefficient versus temperature for a CoGe film.

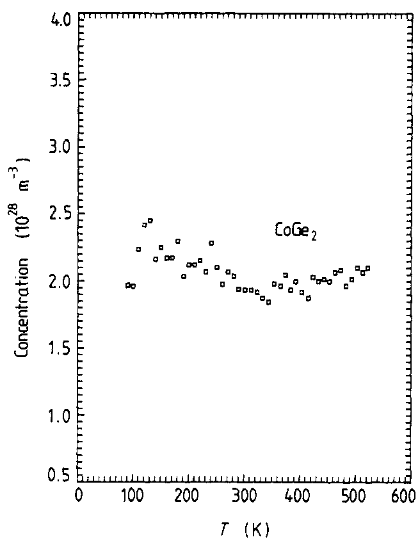

Figure 4. Carrier concentration deduced from the Hall coefficient versus temperature for a $CoGe_2$ film.

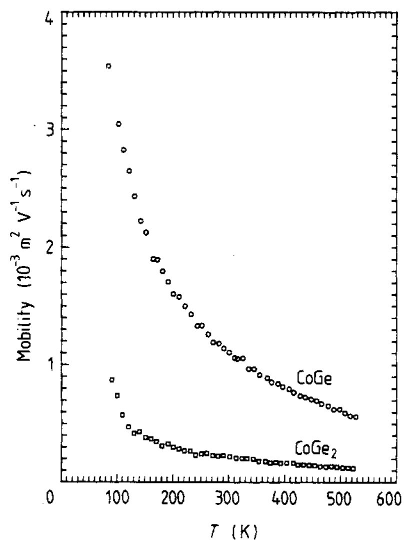

Figure 5. Hall mobility as a function of temperature for CoGe and $CoGe_2$ films.

So, the experimental values of ρ should coincide with the 'bulk' resistivities of the two germanides.

As is shown in figure 1, the resistivity of $CoGe_2$ exhibits a slight deviation from linearity, bending without approaching saturation even at the highest temperatures used in the experiment. On the other hand, $\rho = f(T)$ is linear for CoGe. This difference may be explained by the fact that the mean free path l of the carriers in $CoGe_2$ is about half that in CoGe; as calculated above and for the highest temperatures used, l becomes comparable with the lattice dimensions ($a = b = 5.68$ Å, $c = 10.82$ Å) of $CoGe_2$,

Table 1. Electronic transport parameters derived for CoGe and $CoGe_2$: comparison with CoSi and $CoSi_2$.

	ρ ($\times 10^{-8}$ Ω m)		R_H ($\times 10^{-10}$ m^3 C^{-1})		n ($\times 10^{28}$ m^{-3})		μ ($\times 10^{-4}$ m^2 V^{-1} s^{-1}		
	80 K	300 K	80 K	300 K	80 K	300 K	80 K	300 K	Carrier type
CoGe	22.8	65.7	−8.07	−7.25	0.77	0.86	35.4	11.0	n
$CoGe_2$	29.5	150.0	3.18	3.23	1.96	1.93	10.0	2.2	p
CoSi		147		−62		0.10		43	n
$CoSi_2$	2.5	13.6	2.6	2.1	2.4	3	104	15	p

although it remains larger than the respective dimensions (a = 11.648 Å, b = 3.807 Å, c = 4.945 Å) for CoGe.

In CoGe the sign of the Hall coefficient, as shown in figure 2, reveals that electrons predominate. Also, the apparent carrier concentration, 0.86×10^{28} m^{-3}, at room temperature is very near the value of 0.93×10^{28} m^{-3} calculated with the assumption that there are two mobile electrons per unit cell. This suggests that, if two kinds of carrier contribute to the electrical conduction, holes play only a minor role. The absolute value of the Hall coefficient decreases with increasing temperature, the relative change being 20% for the two extreme temperatures 80 and 530 K. This deviation of the simplified free-electron behaviour, in which R_H is temperature independent, may be attributed to a different change with temperature of the relaxation time characterising the electron scattering between parts of the Fermi surface with different shapes. A similar behaviour of $R_H = f(T)$ observed in noble metals has been explained in this way (Ziman 1961, Alderson *et al* 1968).

As shown in figure 2, the Hall coefficient of $CoGe_2$ is independent of the temperature in the range from 80 to 530 K, as expected for a very simple metal. However, the positive sign of R_H implies that holes are the predominant carriers in this germanide. Moreover, the apparent carrier concentration, 1.93×10^{28} m^{-3}, at room temperature is more than twice the value of 0.86×10^{28} m^{-3} calculated by assuming three carriers per 'molecule'. This discrepancy indicates that carriers of both signs participate more in the conductivity in $CoGe_2$ than in CoGe, a fact that makes R_H smaller and causes an apparent increase in the carrier concentration for $CoGe_2$.

In table 1 some of the transport parameters derived for CoGe and $CoGe_2$ are included together with the similar quantities for the analogous silicides CoSi and $CoSi_2$ for comparison. In both silicides, two carrier types of opposite sign are considered, electrons being dominant in CoSi and holes in $CoSi_2$ (Lien *et al* 1984, Krontiras *et al* 1985).

4. Conclusions

We measured the electrical resistivity and the Hall coefficient for monoclinic CoGe and orthorhombic $CoGe_2$ formed by thin-film reactions, in the temperature range from 80 to 520 K. A metal-like behaviour was revealed for both germanides, with n-type conduction in CoGe and p-type conduction in $CoGe_2$. From the fitting of the $\rho = f(T)$ curves the following parameters were estimated: $\rho_0 = (15 \pm 2) \times 20^{-8}$ Ω m, Θ = 400 ± 10 K and $\rho_\Theta = (90 \pm 2) \times 10^{-8}$ Ω m for CoGe and $\rho_0 = (15 \pm 2) \times 10^{-8}$ Ω m, Θ =

230 ± 20 K and $\rho_\Theta = (150 \pm 5) \times 10^{-8}\ \Omega$ m for $CoGe_2$. A two-carrier type of opposite-sign conduction was revealed by Hall effect curves for both germanides, although greater participation of carriers of both signs in $CoGe_2$ than in CoGe was implied. For a better understanding of the transport properties in germanides the band structure and the Fermi surface topology is necessary.

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