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Intrinsic properties of NiSi

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Abstract

NiSi is a promising material for applications in Si microelectronics. A good understanding of its fundamental physical properties is, however, necessary in order to obtain the best use possible. We present here resistivity, Hall effect and low-temperature specific heat of high quality single crystals. The resistivity of NiSi follows a classical metallic behaviour with a room temperature resistivity of ~ 10 $\mu\Omega$ cm. The Hall coefficient at 300 K is approx. -1.0×10^{-10} m^3 C^{-1}, changes sign at around 40 K and becomes positive: $+0.5 \times 10^{-10}$ m^3 C^{-1} at 4.2 K. Specific heat shows a classical metallic behaviour, i.e. it follows a $\gamma T + \beta T^3$ law with $\gamma = 1.73$ mJ mol^{-1} K^{-2} and $\beta = 0.0317$ mJ mol^{-1} K^{-4}. It also exhibits an anomaly likely of magnetic origin at the lowest temperatures. © 1997 Elsevier Science S.A.

Keywords: NiSi; Resistivity; Hall effect; Specific heat; Si microelectronics

1. Introduction

Some transition metal silicides such as $TiSi_2$ and $CoSi_2$ play an important role in Si-based microelectronics as these compounds possess low electrical resistivities, are immune to electromigration, can be obtained at relatively low temperature on silicon and form highly reproducible Schottky barriers with silicon [1]. Thus they are widely used as contact materials and interconnections. Another possible candidate for such kind of applications is NiSi since it has a low room-temperature resistivity of approx. 10 $\mu\Omega$ cm and can be obtained as high-quality thin films [2]. In order to evaluate its potential for applications it is, however, necessary to examine carefully its intrinsic properties.

NiSi crystallises in an orthorhombic crystal structure (space group Pnma) with lattice parameters a = 5.233 Å, b = 3.258 Å and c = 5.659 Å. We report here resistivity, Hall effect and low-temperature specific heat measurements on single crystals of NiSi.

2. Experimental

Large single crystals of NiSi were obtained by a modified Czochralski pulling technique from a levitated melt in a cold copper crucible [3]. For the transport measurements we obtained two samples of typical dimensions $6 \times 2 \times 0.5$ mm^3 with the longest dimension aligned along the a-axis of the crystal structure. Both samples yield identical results. Transport properties were measured by a four-point AC method in a liquid He cryostat. Magnetic fields ($B \leq 8$ T) were provided by a superconducting coil. We used a transient heat-pulse technique for the measurement of the low-temperature specific heat. Low temperatures (1.6 K < T < 20 K) were achieved with a continuously operating pumped He-4 cryostat.

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3. Results and discussion

The good quality of the crystals was revealed by the high residual resistance ratio RRR = ρ(293 K)/ρ(4.2 K) ≈ 60. The resistivity of NiSi follows Matthiesens law, i.e. it can be described by the sum of a temperature-independent residual resistivity $\rho_0 = 0.16\ \mu\Omega$ cm resulting from the charge carrier scattering by crystal imperfections and impurities and a temperature-dependant resistivity $\rho_i(T) = \rho - \rho_0$ due to electron-phonon scattering. In Fig. 1 we present this temperature-dependent part of the resistivity of NiSi as a function of temperature in a log–log plot. The temperature dependence of the resistivity due to scattering of the charge carriers by phonons can usually be analysed with the Bloch–Grüneisen formula [4]:

$$\rho_i(T) = A\left(\frac{T}{\theta_D}\right)^5 \int_0^{\theta_D/T} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})} \qquad (1)$$

where A is a constant and θ_D is the Debye temperature. A least-square fit according to Eq. (1) is also indicated in Fig. 1 yielding a Debye temperature $\theta_D = 436$ K for NiSi. As one can see in the figure, the data are quite well described by the Bloch–Grüneisen formula over more than four orders of magnitude.

In Fig. 2 we present the low-field Hall coefficient of NiSi as a function of temperature. The Hall coefficient (R_H) is negative at room temperature, thus the dominant charge carriers are electrons and its value $R_H \approx -0.9 \times 10^{-10}$ m^3 C^{-1} corresponds in a simple one-band model, i.e. $R_H = 1/ne$, to a charge carrier density $n = 6.9 \times 10^{28}$ m^{-3}. This result is in good agreement with thin-film data [5]. From room temperature down to approx. 70 K, the Hall coefficient remains nearly constant but at approx. 40 K it changes sign and becomes positive for lower temperatures: $R_H \approx +0.5 \times 10^{-10}$ m^3 C^{-1}. We have already observed a similar behaviour of the Hall coefficient of $TiSi_2$ [6]. This kind of behaviour of the Hall coefficient can be explained with a model of a compensated metal, i.e. charge carriers are electrons and holes with equal numbers, and the two types of carriers are differently affected by the different scattering mechanisms. For a compensated metal it is, however, difficult to deduce a charge carrier density from the Hall coefficient as R_H is given by the superposition of two terms, coming from the different bands [6]. Thus, with the simple one-band model mentioned above, one overestimates the real charge carrier density. Band structure calculations of NiSi [7] confirm that this compound is indeed a compensated metal.

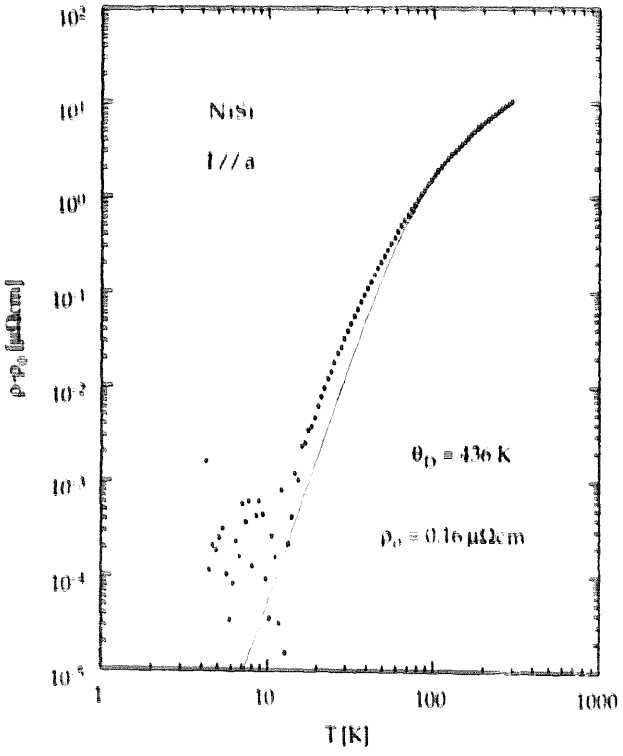

Fig. 1. Temperature-dependent part of the resistivity vs. temperature compared with a fit with the Bloch–Grüneisen formula (Eq. (1), see text).

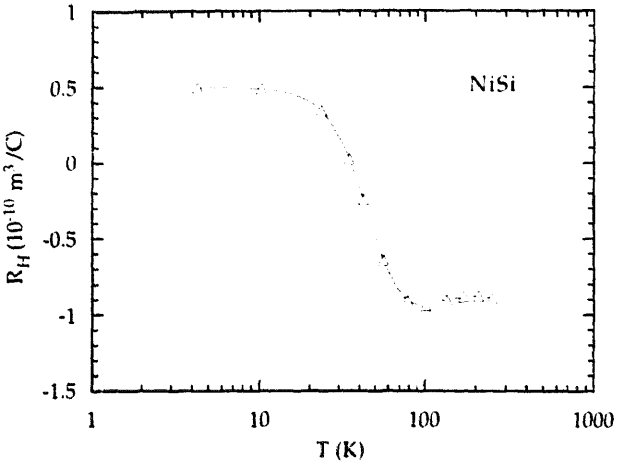

Fig. 2. Low field Hall coefficient of NiSi as a function of temperature. The indicated line is a guide to the eye.

The low-temperature specific heat C_p of NiSi follows a classical metal behaviour, i.e. it can be described by the sum of an electronic contribution γT and a phonon contribution βT^3. In Fig. 3 we present C_p in a C_p/T vs. T^2 plot for the determination of γ and β. The fit was done for the data points below 10 K. From the electronic term γT one can deduce the electronic density of states at the Fermi level $D(E_F)$:

$$D(E_F) = \frac{3\gamma}{\pi^2 k_B^2} \qquad (2)$$

where k_B is the Boltzmann constant. Here we have $\gamma = 1.73$ mJ mol^{-1} K^{-2}, yielding $D(E_F) = 40.5$ states

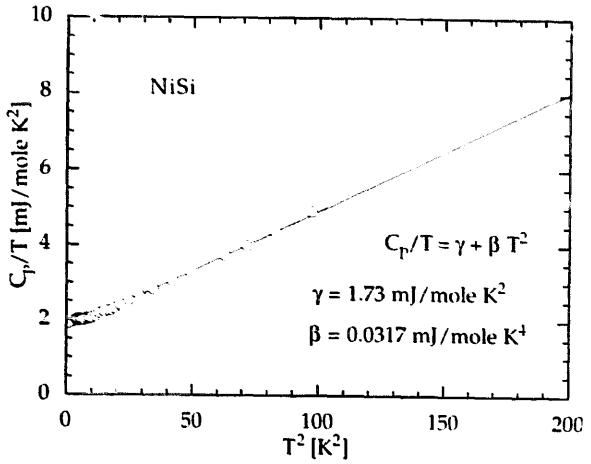

Fig. 3. Specific heat capacity divided by temperature vs. T^2 of NiSi. In the figure we indicate also a fit $C_p/T = \gamma + \beta T^2$ for the determination of γ and β (see text).

per Ry unit cell. Theoretical band structure calculations [7] predict a γ-value of 1.3 mJ mol^{-1} K^{-2} corresponding to $D(E_F) = 30$ states per Ry unit cell, in good agreement with our experimental result.

From the lattice contribution to the specific heat βT^3, we can deduce the Debye temperature of NiSi:

$$\theta_D = 3\sqrt{r\frac{12}{5}\frac{R\pi^4}{\beta}} \quad (3)$$

where R is the gas constant and $r = 2$ atoms/molecule. With $\beta = 0.0317$ mJ mol^{-1} K^{-4} this yields $\theta_D = 497$ K, a value higher than the Debye temperature found by the resistivity analysis. This difference in the two values of Debye temperatures probably results from the fact that the explored temperature regions for the determination of θ_D were not the same (specific heat: 1.6 K $\leq T \leq$ 10 K; resistivity: 4.2 K $\leq T \leq$ 300 K). In Fig. 3 one can see two deviations from the classical $\gamma T + \beta T^3$ law: At high temperatures ($T >$ 10 K) higher order terms in T lead to a curvature of the data curve. At lowest temperatures ($T \leq$ 3 K) we observe a significant deviation from the $\gamma T + \beta T^3$ law. This latter feature is likely of magnetic origin, but we have insufficient experimental data to confirm these results up to now.

The magnetic susceptibility measured on NiSi single crystals is similar to those already found for the group 5 disilicides [8]. NiSi is diamagnetic at high fields (0.2 T < B < 7 T), due to the core diamagnetism of the metal ions. At low temperatures and low magnetic field, however, one can observe a curvature in the magnetisation vs. applied magnetic field curve. It is not surprising that some magnetic effects can be observed in NiSi as the related compounds FeSi and CoSi [9] show a strong paramagnetism and moreover MnSi orders antiferromagnetically at low temperatures [10].

4. Conclusions

We have measured the resistivity, the Hall effect and the low-temperature specific heat of single crystalline NiSi. We found a room temperature resistivity of approx. 10 $\mu\Omega$ cm as already reported for thin films. Hall-effect measurements and band-structure calculations indicate that this monosilicide is a compensated metal. From the low-temperature specific heat measurements we deduced the electronic density of states at the Fermi level and the Debye temperature for this compound. Some magnetic effects were observed at low temperature and we will continue our investigations in order to clarify this point.

Acknowledgements

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