RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 44, NUMBER 23 15 DECEMBER 1991-I

Quantum size effects and grain-boundary scattering in polycrystalline cobalt disilicide films

R. G. P. van der Kraan, J. F. Jongste, H. M. Jaeger,* G. C. A. M. Janssen, and S. Radelaar
Delft Institute for Microelectronics and Submicron Technology, Delft University of Technology, 2600 GA Delft, The Netherlands
(Received 22 July 1991)

We have investigated the effective contributions from surface and grain-boundary scattering to the overall resistivity in the quantum-transport regime in ultrathin $CoSi_2$ metal films ranging from 2 to 300 nm in thickness. Grain boundaries were introduced by growing the films on Si(100) substrates. We find a clear crossover between two types of behavior as the film thickness is decreased. Down to 10 nm size effects on the resistivity are weak and the data are best approximated by grain-boundary scattering using the experimentally determined dependence of grain size on thickness. Below 10 nm the data approaches a power law $\rho \propto d^{-2.0}$ as surface scattering due to quantum size effects starts to dominate.

In very thin metal films size effects lead to phenomena not observed in bulk transport behavior. For film thicknesses comparable to the electronic mean free path, material parameters like the resistivity, which by definition are geometry independent in the bulk, acquire a size dependence due to the increasing importance of scattering contributions from the film's surfaces. Traditionally, the observed increase of the resistivity with decreasing thickness has been interpreted within the Fuchs-Sondheimer theory,[1] which dates back to the 1930's. In this semiclassical theory size-effect contributions to the resistivity, ρ, arise from diffuse surface scattering events when the ratio of film thickness to electronic mean free path, d/l, becomes small. However, even in the presence of completely diffuse surface scattering the resistivity increase predicted by the semiclassical treatment can be arbitrarily small if only l is large enough. This result is in contradiction with recent data on ultrathin metal films, in particular epitaxially grown ultrathin $CoSi_2$ films,[2-5] which exhibit a substantial size effect on the resistivity despite a large mean free path and predominantly specular surface scattering. This has led to the development of surface scattering theories[6-8] that explicitly take the quantum nature of electron transport in ultrathin films into account. These approaches show that there are quantum size effects which lead to a resistivity increase even for perfect, specularly reflecting film surfaces.[9] So far these models have been applied to single-crystal films where surface scattering presumably is the dominant mechanism. In general, however, additional scattering mechanisms are present even when the impurity mean free path l is very long. A key question thus concerns the relative strengths of quantum size effects, i.e., to what extent the resistivity enhancement in the ultrathin-film limit might survive as a general signature of quantum size effects.

One important example of additional scattering sources is grain boundaries. A detailed understanding of the effective contributions from surface and grain-boundary scattering to the overall resistivity in the quantum transport regime in metal films presently is lacking. We report here on a systematic experimental investigation of this issue in ultrathin $CoSi_2$ films ranging from 2 to 200 nm in thickness where grain boundaries were introduced by growing the films on Si(100) substrates. The resulting polycrystalline $CoSi_2$ films form a model system for such a study because individual grains retain the surface quality at the interfaces and the high degree of specular scattering found in epitaxial films grown on Si(111). Our results show a clear crossover between two types of behavior as the film thickness is decreased: down to about 10 nm size effects on $\rho(d)$ lead to a relatively weak increase in resistivity and the data are best approximated by grain-boundary scattering using the experimentally determined dependence of grain size on thickness. Below 10 nm the data approach a power law $\rho \propto d^{-2.0}$ as surface scattering due to quantum size effects begins to dominate.

Metal silicides have been intensively studied in recent years because of the possibility to grow continuous, ultrathin layers on silicon which exhibit atomically sharp interfaces. Cobalt disilicide, $CoSi_2$, has been of particular interest because of its relatively low residual resistivity (2.5 $\mu\Omega$ cm) and its very small lattice mismatch (1.2%) with the Si(111) surface. This has allowed epitaxial growth of continuous, metallic $CoSi_2$ films on Si(111) with thicknesses down to 1 nm.[3]

We have fabricated polycrystalline $CoSi_2$ films by Co sputter deposition on Si(100) substrates followed by annealing in an argon atmosphere at 700 °C for 10–120 s, depending on the layer thickness. During the anneal, performed in a rapid thermal processor, the Co is transformed to $CoSi_2$ as verified by x-ray diffraction. To define a suitable film pattern for electrical measurements (two current leads and several voltage probes) a self-aligned silicide process[10] was utilized. In this process prior to Co deposition the wafer was oxydized, the pattern transferred into the oxide by photolithography and the oxide under the pattern removed by wet etching. After Co sputtering $CoSi_2$ formed selectively in the areas not covered by SiO_2. A final step was the removal of unreacted Co on top of SiO_2 by wet etching. The patterned film strips were 400 μm wide with a spacing of 2000 μm between voltage probes.

The nominal layer thickness of all films was determined from the sputter time which was calibrated by Rutherford-backscattering measurements and showed excellent linearity. Cross sections of several of the thinnest films were later analyzed by high-resolution transmission electron microscopy (HREM).[11] The HREM pictures clearly revealed the presence of grains with different crystal orientations. Epitaxially grown grains were predominantly oriented along the Si(111) direction. All grains typically exhibited an almost perfectly flat top surface. Any roughness, if at all discernable, occurred on a scale of single atoms. The bottom surface, i.e., the $CoSi_2$/Si interface, on the other hand, in many cases was rough on longer scales (≈ 10 nm) with steps of one to several atomic layers in height. Electron spectroscopy for chemical analysis and Auger electron spectroscopy indicated the presence of a thin (1 nm) SiO_2 layer on top of the films.

Figure 1 shows the measured residual resistivity as a function of nominal film thickness. The measurements were performed at 4.2 K using standard lock-in techniques. Except for a 1-nm-thick sample all films were electrically continuous and metallic ($d\rho/dT > 0$ for $T > 4.2$ K). The measured resistivity at thicknesses below 10 nm compares very well with data taken by Phillips *et al.*[3] on epitaxial layers grown on Si(111). Furthermore, in the limit of large $d > 200$ nm we find a bulk resistivity value $\rho_{0\infty} = 2.2\ \mu\Omega\,\text{cm}$ which is within the range of previously reported values for epitaxial films. This bulk resistivity, due to impurity scattering, translates[12] into an electronic mean free path of 43 nm. Both results indicate a degree of specular surface scattering in our polycrystalline films comparable to that of epitaxially grown films.

The effect of the polycrystallinity on the resistivity can be modeled by the grain-boundary scattering theory of Mayadas and co-workers.[13] Grain boundaries in this semiclassical approach are represented by a sequence of partially reflecting parallel walls with reflection coefficient R, separated by a random distance, the grain diameter, which is taken to have a Gaussian distribution around its mean value, D. This is essentially a one-dimensional model of δ-function barriers perpendicular to the direction of current flow. It is particularly appropriate for columnar grain growth,[14] as in the case of $CoSi_2$. The resulting background resistivity ρ_0 due to grain-boundary scattering is expressed as

$$\frac{\rho_{0\infty}}{\rho_0} = 1 - \tfrac{3}{2}\alpha + 3\alpha^2 - 3\alpha^3 \ln\left[1 + \frac{1}{\alpha}\right], \tag{1}$$

where the parameter $\alpha = (l/D)R(1-R)^{-1}$. Following de Vries,[15] Eq. (1) can be approximated by $\rho_{0\infty}/\rho_0 = (1 + 1.39\alpha)^{-1}$ to within a few percent over the range of experimental data relevant here. This leads to the linear relationship $\rho_0 D = \rho_{0\infty} D + c$, where $c = 1.39\rho_{0\infty} l R(1-R)^{-1}$, and allows to determine the reflectivity parameter R from a plot of $\rho_0 D$ as function of D. For grain sizes much larger than 10 nm, where the grain-boundary scattering is not dominated by quantum size effects and therefore ρ essentially is given by ρ_0, we find $c = 2.3 \times 10^{-5}\ \mu\Omega\,\text{cm}^2$. This leads to a reflection coefficient $R = 0.63$, confirming the picture of highly reflecting grain surfaces as well as side walls.

In order to directly determine the thickness dependence of the grain-boundary contribution to the overall resistivity the boundaries were made visible for scanning electron microscopy (SEM) by selective wet etching. Due to the columnar grain growth in $CoSi_2$, a short etch resulted in a V-shaped groove along the boundary. The average diameter D was then determined from histograms of the grain size distributions and is shown in Fig. 2. Using these data to calculate $\alpha(d)$ in Eq. (1) gives the dashed curve in Fig. 1. We find that the grain-boundary scattering model provides an excellent fit to the data down to about 10-nm film thickness accounting for the initial twofold to threefold increase in resistivity as d is reduced.

It should be noted that a fit to the data above 10 nm can also be obtained with the Fuchs-Sondheimer theory if completely diffuse surface scattering is assumed. However, completely diffuse surface scattering is in direct contradiction to the high degree (90%) of specular scattering found[16] in epitaxial $CoSi_2$ films. Furthermore, Mayadas and co-workers[13] showed that grain-boundary scattering can be erroneously interpreted to follow the Fuchs-Sondheimer theory by assuming an inflated proportion of diffuse surface scattering.

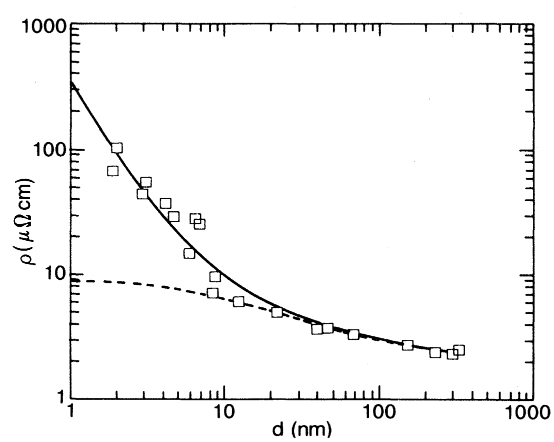

FIG. 1. Residual resistivity measured at 4.2 K as a function of film thickness. The dashed curve gives the prediction of the grain-boundary scattering model by Mayadas and co-workers (Ref. 13). The solid curve interpolates between the dominant contributions to the resistivity of grain-boundary scattering at large thicknesses and power-law behavior due to quantum size effects for the thinnest films (see Fig. 3).

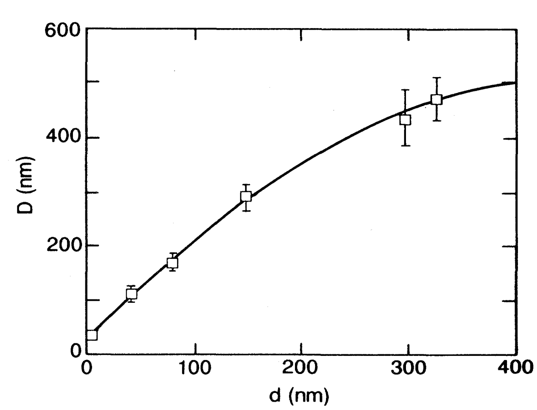

FIG. 2. Average grain diameter D as a function of film thickness d.

For the thinner films the total resistivity in Fig. 1 by far exceeds the grain-boundary scattering resistivity ρ_0 (as well as the Fuchs-Sondheimer theory, which only gives a maximum increase of less than tenfold). After subtraction of the grain-boundary contribution the excess resistivity $\rho_s = \rho - \rho_0$ follows a power law $\rho_s \propto d^{-\alpha}$ as shown in Fig. 3 with a best fit $\alpha = 2.0$. Although in the thinnest films we can determine the presence of pinholes from the HREM pictures,[11] fitting the data to a percolation model shows that the pinhole coverage is too low and its dependence on thickness too weak to explain the upturn in $\rho(d)$ as d is decreased below 10 nm. Below 2 nm, on the other hand, the films appear to break up into isolated islands and 1-nm-thick samples were no longer electrically continuous.

Power-law behavior with an exponent close to two is predicted to arise from quantum size effects where the confinement of electrons by the surfaces of an ultrathin film leads to a set of discrete energy levels. Surface roughness is then modeled by random variations in the confining potential. Since in metal films typically many subbands are occupied, surface scattering results in intersubband transitions which lead to contributions to the resistivity. This general scenario is common to all the recent approaches by Tesanovic, Jaric, and Maekawa,[6] Trivedi and Ashcroft,[8] as well as Fishman and Calecki.[7] A power law $\rho_s \propto d^{-\alpha}$ with $\alpha = 2$ is derived by the first two groups whose models consider the rms magnitude Δ of the surface roughness. The theory by Fishman and Calecki,[7] in addition, includes a surface roughness correlation length ξ. A power law with $\alpha = 2.1$, independent of adjustable parameters, results as a limiting expression with is applicable for ξ of order one Angstrom and a large number of occupied subbands N. This is quite reasonable for ultrathin $CoSi_2$ films with atomic scale roughness where N varies from 3 to 60 in the thickness range 1–20 nm. For larger ξ the exponent α decreases slowly reaching 1.9 at $\xi \approx 5$ Å.[17] Since this roughness correlation length in all cases is much shorter than the grain diameter, the finite size of individual grains is not expected to have significant influence on the surface scattering contribution. Thus while the polycrystallinity affects the longer-range grain-boundary scattering portion, the very short-range correlations responsible for the quantum scattering contribution remain unchanged.

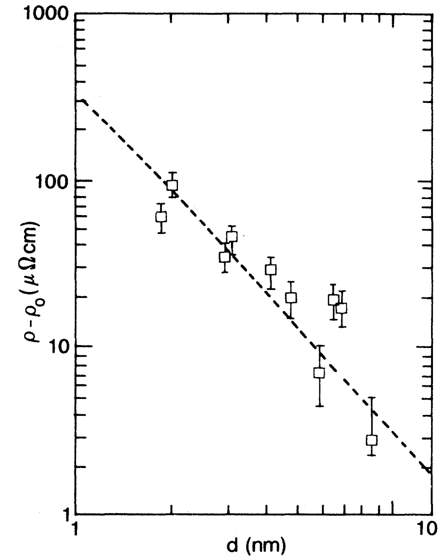

FIG. 3. Excess resistivity $\rho_s = \rho - \rho_0$, i.e., after subtraction of the grain-boundary scattering contribution ρ_0, vs film thickness d. The dashed line indicates the power-law behavior $\rho_s \propto d^{-2}$ predicted by quantum surface scattering models (Refs. 6–8).

In conclusion, we have fabricated ultrathin polycrystalline $CoSi_2$ films which are metallic and electrically continuous down to 2-nm thickness. Measurements of the thickness-dependent resistivity indicate that quantum size effects in $CoSi_2$ survive in the presence of grain-boundary scattering. The observed power law for the resistivity is in very good agreement with theory provided that the thickness-dependent grain-boundary scattering contribution has been subtracted.

This work was part of the research program of the IOP-IC and the "Stichting voor Fundamenteel Onderzoek der Materie (FOM)," which is financially supported by the "Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO)." We wish to thank G. Leusink for stimulating discussions and P. F. A. Alkemade, O. B. Loopstra, S. Roorda, W. G. Sloof, and H. W. Zandbergen for their assistance with the film characterization.

*Present address: The James Franck Institute and Department of Physics, The University of Chicago, 5640 South Ellis Avenue, Chicago, IL 60637.

[1]K. Fuchs, Proc. Cambridge Philos. Soc. **34**, 100 (1938); E. H. Sondheimer, Adv. Phys. **1**, 1 (1952).

[2]P. A. Badoz, A. Briggs, E. Rosencher, F. Arnaud d'Avitaya, and C. d'Anterroches, Appl. Phys. Lett. **51**, 169 (1987).

[3]Julia M. Phillips, J. L. Batstone, J. C. Hensel, and M. Cerullo, Appl. Phys. Lett. **51**, 1895 (1987).

[4]J. Y. Duboz, P. A. Badoz, E. Rosencher, J. Henz, M. Ospelt, H. von Känel, and A. Briggs, Appl. Phys. Lett. **53**, 788 (1988).

[5]J. Henz, J. Hugi, M. Ospelt, and H. von Känel, Surf. Sci. **228**, 9 (1990).

[6]Zlatko Tesanovic, Marko V. Jaric, and Sadamichi Maekawa, Phys. Rev. Lett. **57**, 2760 (1986).

[7]Guy Fishman and Daniel Calecki, Phys. Rev. Lett. **62**, 1302 (1989).

[8]Nandini Trivedi and N. W. Ashcroft, Phys. Rev. B **38**, 12 298 (1988).

[9]Other manifestations of quantum size effects include oscillations of the transition temperature as function of thickness in superconducting films. See Ref. 8 and B. G. Orr, H. M. Jaeger, and A. M. Goldman, Phys. Rev. Lett. **53**, 2046 (1984).

[10]L. van den Hove, J. Vac. Sci. Technol. B **4**, 1358 (1986).

[11]R. G. P. van der Kraan, J. F. Jongste, G. C. A. M. Janssen, and S. Radelaar (unpublished).

[12]L. F. Matteiss and D. R. Hamann, Phys. Rev. B **37**, 10623 (1988).
[13]A. F. Mayadas, M. Shatzkes, and J. F. Janak, Appl. Phys. Lett. **14**, 345 (1969); A. F. Mayadas and M. Shatzkes, Phys. Rev. B **1**, 1382 (1970).
[14]A. E. Morgan, R. K. Broadbent, M. Delfino, B. Coulman, and D. K. Sadana, J. Electrochem. Soc. **134**, 925 (1987).
[15]J. W. C. de Vries, Thin Solid Films **167**, 25 (1988).
[16]J. C. Hensel, R. T. Tung, J. M. Poate, and F. C. Unterwald, Phys. Rev. Lett. **54**, 1840 (1985).
[17]D. Calecki and G. Fishman, Surf. Sci. **229**, 110 (1990).