Cryst. Res. Technol. **41**, No. 5, 458 – 463 (2006) / **DOI 10.1002/crat.200510605**

Thin overlayer influence on electrophysical properties of nickel films

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Received 13 June 2005, accepted 17 July 2005

Key words thin films, resistivity, temperature coefficient of resistance, reflection coefficient, grain boundary, transmission coefficient, reflectivity.
PACS 68.55.Nq

In this work it is experimentally investigated a size effect in temperature coefficient of resistance (TCR) of Ni films with Cu and SiO_2 thin overlayer. The parameters of electrical transfer (the mean-free path of electron, the reflectivity coefficient of the external surfaces, the reflection and transmission coefficients at the grain boundary) were calculations. Decreasing of the value of the reflectivity coefficient is due to the change of the surface microrelief. It is show that the value of TCR decreases caused by the conditions of scattering changes on internal and external boundaries.

1 Introduction

Influence of overlayer on electronic transport in multilayer metal films has attracted a lot of attention in the last few decades. The size-dependent electrical resistivity and temperature coefficient of resistance (TCR) of as-deposited and annealed atomic beam-deposited polycrystalline copper films of 20 nm with chromium underlayer was measured [1]. It was shown the TCR of Cu films decreases with the chromium thickness to reach a minimum value at about $d_{Cr} = 1$ nm.

The interlayer surface scattering was investigated by David et al. [2] for the case of layered structure consisting of Cu and Co films coated with Co (or Cu, respectively). The films were epitaxially grown on Si(111) substrate. They reported the non-monotonic behavior of the structure resistance with the thickness of capping Co layer. Initially, the resistance increases but it turns to decrease when one or more Co monolayers have been formed. The physical reason of the initial increase is appearing of Co islands on the surface of a cupper film. A different situation arises when Co film was coated with Cu. Upon deposition of Cu atoms on a cobalt surface, no facts of the island nucleation were observed. Consequently, in this case, the resistance does not increase with thickness of the capping Cu layer.

The kinetics on polymer layer growth on the surface of a single-crystal Cu(100) film has been studied [3]. The combination of in situ d.c.-resistance measurements and simultaneous of the non-resonant infrared reflectance provides a sensitive, noninvasive, real-time probe of adsorption kinetics on thin metal films. The two techniques are complementary, with the resistance sensitive to first-layer adsorption while the reflectance shows effects due to both first-layer and multilayer adsorption. It was demonstrated that the formation of the first polymer monolayer (at 125K) leads to a two-percent increase of the electrical resistance of the Cu film. While the reflection coefficient degraded on a half of a percent. The detailed analysis of these measurements proved both the increase of the resistance (of the order of a few percent) and degradation of the reflection coefficient is due to the formation of islands on the film surface. Note, the resistance does not increase appreciably with the coalescence of islands into monolayer and with further formation of the next layers. Small increase of the electrical resistance, presumably, is due to the reducing of the probability of specular reflection at the external surface.

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The detailed theoretical analysis of the scattering processes of charge carriers at metal film surfaces was performed by Panchenco and Sologub [4]. They pointed out that a real single crystal has surface damages; furthermore, contaminants coat its surface. Consequently, a periodical surface microrelief is disturbed. It is the reason (among other properties of a real crystal surface) which is responsible for the increase of a probability of the diffusive surface scattering. Thus, coating an island Ag layer on to the thin tungsten film W(100) leads to increase of its' magnetoresistance due to the lack of specular reflection at the external surface.

In summary, the analysis of the aforementioned papers [1–4] demonstrates that the characteristics of the surface scattering in thin films may be affected essentially due to the coating with foreign atoms on to the film surface. Usually, this results in reducing of specular reflection from surfaces.

Under certain conditions of heat treating, atoms of a thin coating layer will diffuse into the basic layer. While the bulk electrical resistance of the film (which is caused mainly by the electron-phonon scattering) remains almost constant under the grain-boundary diffusion, the grain-boundary resistance may be changed essentially due to the localization of foreign atoms on the grain boundaries [5].

Here, we should note the following fact. The theoretical treatment of the electron transmission through the interface between one-dimensional metal crystals performed by Braginskij and Romanov [6] demonstrates that the effect of foreign atoms on the grain boundaries is ambiguous. These atoms may cause either the increase or the decrease of transparency of the grain boundaries. Consequently, the grain boundaries can turn either highly scattering or highly transparent. Thus, as it was demonstrated by Protsenko et al. [7], the coefficient of the grain-boundary scattering in Ni and Cr films decreases after the coating with Ge layer which thickness is less than 10 nm. This result can be explained by healing of defects at the grain boundaries by coated atoms.

In view of existing interest to the role of overlayer in the electron transport properties of thin films, it seems reasonable to study this issue in details. We investigate experimentally the effect of coating with Cu and SiO_2 on to the Ni films and subsequent changes in the parameters of electron transport. We studied the coefficient of the specular reflection from the outer surface, the coefficients of the grain boundary scattering and grain boundary transmission under the conditions when atoms and molecules of the capping layer may diffuse into the basic layer or they do not make this migration.

2 Theoretical model and approximations

Various model for thin films exist to understand the contribution from different scattering mechanisms, namely (i) bulk scattering; (ii) surface scattering, and (iii) grain-boundary scattering which may be predominant in polycrystalline films. A widely-used model was proposed by Mayadas and Shatzkes [8]. They take into account the scattering at grain boundaries in thin metal films. The model operates with the specularity coefficient p, which describes the surface scattering, and the grain boundaries parameter $\alpha = \lambda R / \left(L(1-R) \right)$ which determines the characteristic properties of the electron scattering at the grain boundaries (where λ is electron mean-free path (m.f.p.) in by materials, R is a probability of specular reflection from the grain boundaries and L is the average crystallite size). Unfortunately, the general formulas of the Mayadas and Shatzkes model provide no possibilities for direct comparison between experimental data and theory. To determine the parameters of the electron transport we use both the linearized model (which is the approximation of the Mayadas and Shatzkes model) and the isotropic model proposed by Tellier, Tosser and Pichard [9].

Within the linearized model, the temperature coefficient of resistance, β, is given by

$$\beta \cdot d \cong \beta_\infty \cdot d - \beta_\infty \cdot \lambda \ (1-p) H(\alpha) , \tag{1}$$

here $\beta_\infty = \lim\limits_{d \to \infty} \beta$, d is the film thickness and function $H(\alpha)$ is determined by the grain boundaries parameter [9].

Within the isotropic model, the TCR of a film may be written as

$$\beta^{-1} \cdot d \cong \beta_\infty^{-1} \cdot d + \frac{3}{8} \beta_0^{-1} \lambda \ \ln\left(p^{-1}\right) , \tag{2}$$

$$\beta_\infty \cdot \beta_0^{-1} \cong \left[1 + 1,45 L^{-1} \lambda \ln\left(r^{-1}\right) \right]^{-1} , \tag{3}$$

$$R(1-R)^{-1} \cong 0{,}97\ln\left(r^{-1}\right), \qquad (4)$$

where β_0 is the TCR of a bulk sample and r is the coefficient of the transmission through the grain boundary.

To determine the parameters of the electron transport (i.e. p, r, R, λ) we need to rebuild our experimental data as functions of the parameters that used in the theoretical models. Thus, to examine the linearized model we rebuilt our experimental dependence of the TCR vs. film thickness d to the plot βd vs. d. In this case, the slope of the experimental curve should correspond to the value of β_∞, and the ordinate axis intercept should corresponds to the value of $\beta_\infty \cdot \lambda(1-p)H(\alpha)$. In the case of the isotropic model, we need plot experimental values as $\beta^{-1}d$ vs. d. Consequently, the slope of the experimental curve should correspond to the value of β_∞^{-1} and the ordinate axis intercept should correspond to the value of $\frac{3}{8}\beta_0^{-1}\lambda\ln\left(p^{-1}\right)$. With a knowledge of the average grain size one may use aforementioned data to calculate the electron transport parameters.

3 Experimental technique

The Ni thin films were grown on polycore substrates. The substrate temperature T_S was kept at 460-470K during the deposition process, that is close to the Debye temperature of bulk Ni. According to Schummacher and Stark [10], this temperature regime provides a minimum of lattice defects under crystallization. The certain configuration of contact pad of Cu (150-200nm)/Cr (30-50nm)/S (Substrate) were deposited thermally. This allows both simultaneous obtaining of three identical Ni films and measuring their electrical properties. One of the films was kept uncapped; this film was used as a control sample under the investigation of electrical transport in the rest two capped films. To measure the electrical resistance we used Nichrome pressed contacts. After deposition, our structure was cooled down to the room temperature and two sequential heating-cooling cycles (in the temperature range 300-630K) were made. At the next stage, the rest two films were capped with Cu and SiO_2 layers, respectively, at the temperature T_s=300K. The thickness of the capped layers, $d \leq 1$ - 2 nm. Then the heating-cooling cycle was repeated for the third time and samples were cooled down to T_S = 100K in a vacuum.

The average grain size, L, was calculated by using the data of transmission electron microscopy for Ni films of different thicknesses. Figure 1 shows a thickness dependence of the average grain size. We use the data at calculation of the parameters of electron transport. The experiments on electron diffraction demonstrated that Ni films have a fcc lattice structure with a period which is approximately equal to the period of bulk Ni.

4 Experimental results and discussion

Figure 2 shows typical temperature dependences of the resistivity, $\rho(T)$, measured for the third heating-cooling cycle. Initially, the resistivity of the thin Ni film diminishes slightly (of the order of 0.1 - 0.2 percent) due to the coating with Cu. However, the resistivity of the layered system Cu/Ni/S increases essentially after the heat treatment, when system turns to be thermally stable. Depending on the basic-layer thickness, the increase is of the order of 10 - 20 percent.

Let us discuss some results. Upon cooling Ni films overlayer Cu from 400 K down to 300 K, we found that the slope $\Delta\rho/\Delta T$ is larger than a corresponding value for the non-coated Ni film. Upon cooling Ni films overlayer SiO_2, we found that the curve $\rho(T)$ lies below to the corresponding curve for the non-coated Ni film. In this case, the value of the slope, $\Delta\rho/\Delta T$, increases at heating and decreases at subsequent cooling in comparison with the slope of the corresponding temperature of the resistivity of the non-coated Ni film (the difference is of the order 0.4 – 0.7 percent).

Figure 3 show the size dependencies of the TCR, $\beta \equiv (1/\rho)(\partial\rho/\partial T)$, calculated at temperatures 100, 300 and 550K. Note, calculating the TCR we exclude the temperature intervals both near the Debye temperature (Θ_{0D} = 465K) and near the Curie temperature (Θ_{0C} = 631K [11]). Here we should note, the role of the Curie temperature is very important for the temperature-dependent scattering and the TCR both in thin and bulk samples [12]. Note, a depression both of the Debye temperature and of the Curie temperature with the film thickness was observed early. In two-layer films, the concentration effects also affect these characteristic temperatures, as it was discussed [13]. In the vicinity of Θ_C we found well-pronounced changes of the behavior of the temperature dependence both for the SiO_2/Ni/S and for the Ni/S films as shown in figure 2. While, there is no sharp changes of the temperature dependence for the resistivity of the Cu/Ni/S film.

Thus, the TCR of thin Ni films reduces due to the coating with Cu and SiO_2 as it follows from results presented in figure 3. Moreover, overlayer Cu affect the TCR most effectively.

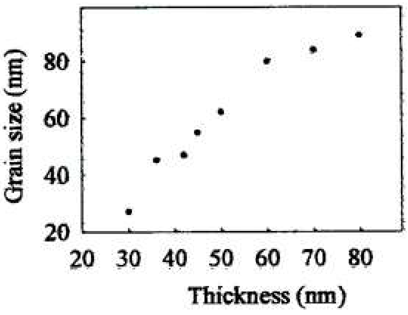

Fig. 1 Thickness dependence of the average grain size in Ni films.

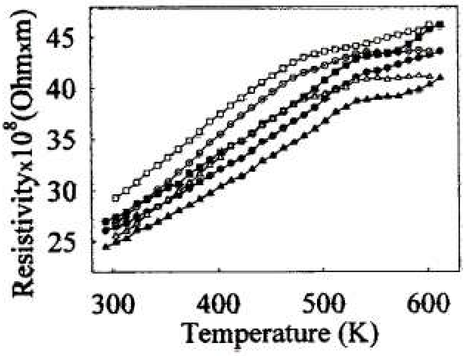

Fig. 2 Temperature dependence of the resistivity $\rho(T)$ for: (i) uncoated Ni films of d=30nm thickness (●, heating; ○, cooling); (ii) Ni films coated with Cu (■, heating; □, cooling); and (iii) Ni films coated with SiO_2 (▲, heating; △, cooling) at the third annealing cycle.

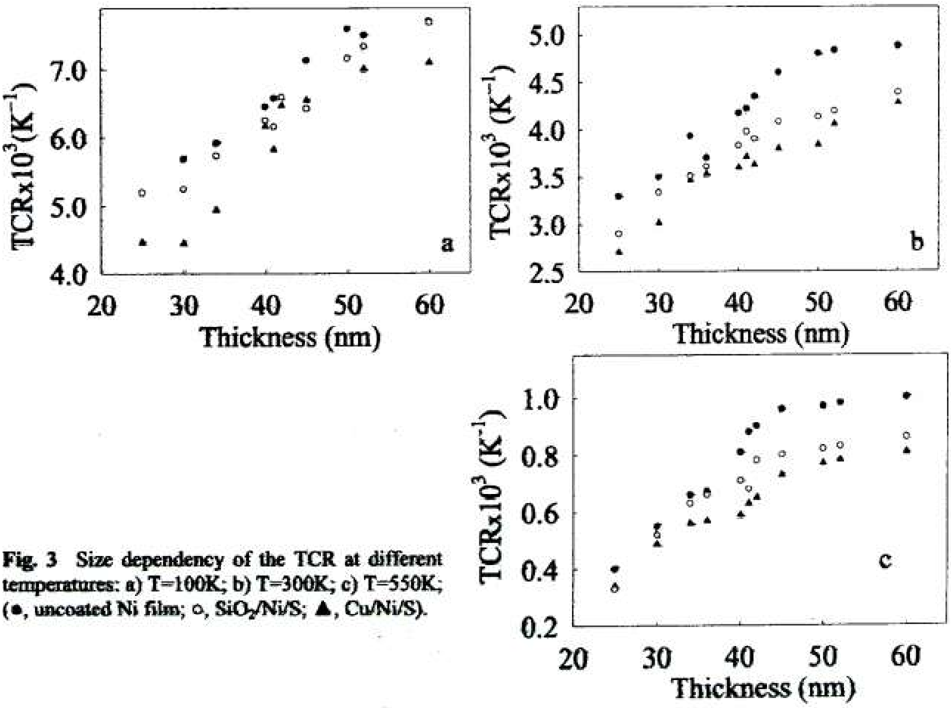

Fig. 3 Size dependency of the TCR at different temperatures: a) T=100K; b) T=300K; c) T=550K; (●, uncoated Ni film; ○, SiO_2/Ni/S; ▲, Cu/Ni/S).

Let us turn to calculation of the electron transport parameters p, r and R. We suppose that overlayer Cu and SiO_2 do not change the bulk electron mean free path in Ni films but it changes the electron scattering at the grain boundaries and external layer surfaces. Within the linearized model (see Eq.(1)), we calculate m.f.p. at different temperatures and obtain the following values: 42.6 nm at 100K, 28.7 nm at 300K, and 26.9 nm at 550K. These values of the m.f.p. we use to estimate the electron transport parameters within the isotropic model. Table 1 summarizes this result and includes the percentage changes in the parameters of overlayer films with respect to the parameters of uncoated films.

Table 1 Results of calculation of the parameters of electron transport.

T, K	Films	p	R	r	$\left\|\frac{\Delta p}{p}\right\|$,%	$\left\|\frac{\Delta r}{r}\right\|$,%
100	Ni/S	0.26	0.09-0.16	0.90-0.82	-	-
	Cu/Ni/S	0.18	0.12-0.21	0.87-0.76	30.8	3.3-7.3
	SiO_2/Ni/S	0.22	0.10-0.19	0.89-0.79	15.4	1.1-3.7
300	Ni/S	0.19	0.01-0.03	0.98-0.96	-	-
	Cu/Ni/S	0.10	0.03-0.06	0.96-0.93	47.4	2.0-3.1
	SiO_2/Ni/S	0.11	0.02-0.04	0.97-0.95	42.1	1.0-1.1
550	Ni/S	0.21	0.03-0.06	0.96-0.93	-	-
	Cu/Ni/S	0.06	0.11-0.20	0.87-0.77	71.4	9.4-17.2
	SiO_2/Ni/S	0.09	0.07-0.13	0.92-0.86	57.0	4.2-7.5

The value of the coefficient of the specular reflection from the external surface decreased when outer Cu (or SiO_2) layer has been coated. In agreement with results of Panchenco and Sologub [4], we explain this fact by the changes in surface microrelief, which lead to the degradation of the probability of specular reflection from the external surface. The grain-boundary transparency degrades due to the diffusion of Cu atoms along the grain boundaries into the Ni film. Presumably, the diffusion of the foreign atoms in our samples leads to appearing additional defects at the grain boundaries. The coefficient of the grain-boundary scattering also increases when Ni film coated with SiO_2, but the increase is not as strong as in the foregoing case. We suppose that it may explained by the diffusion of a few number of Si atoms along the grain boundaries into Ni and appearing of a small quantity of the nickel silicide. Note, SiO_2 is a very stable compound. The next reason that could explain our result is the following. It is impossible to separate the effects of the surface and grain-boundary scattering in the TCR when we based on the Eqs. (2) – (4) only.

Below we discuss briefly some issues related to the model of the grain boundary transmission. Following to Mayadas and Shatzkes [8] one may introduce the "strength" of the potential at grain boundaries, viz. *S*. Physically, *S* is approximately equal to the height of the potential barrier multiplied by its width. *S* may be expressed in terms of the scattering coefficient, *R*, via the following proportion [8]

$$S^2 \sim R(1-R)^{-1}. \tag{5}$$

It was assumed that concentration of dislocations, impurity atoms, defects etc. at the grain boundaries leads to appearing of localized energy levels at grain surfaces and, consequently, an effective charge Q^* of the density ρ_q^*. Solving the Poisson equation in the case of spherical grains [14] have obtained the following formulas for the "strength" of the potential

$$S = -\frac{\rho_q^* L^2 \delta L}{24\varepsilon'}, \tag{6}$$

where $\varepsilon' = \varepsilon\varepsilon_0$ is the absolute dielectric constant.

Using Eqs. (5) and (6) we obtain the following result (assuming that $R < 0.3$)

$$R \sim \rho_q^{*2} L^4 (\delta L)^2 \sim Q^{*2}. \tag{7}$$

Thus, the value of coefficient of the grain boundaries scattering increases with increasing of the surface density of charge. Consequently, we may expect that the grain boundaries scattering increases when foreign impurities absorbed at the grain boundaries have increased the value of the surface charge Q^*. It is possible also, that effect of foreign impurities may reduce the initial value of Q^*. Therefore, one may control the electron transport in layered films through the choice of the certain capping materials. Noticeably, both the resistivity and the temperature coefficient of resistance may be either increased or decreased in this way.

5 Conclusion

In summary, we have investigated the electron transport properties of thin Ni films and the effects of overlayer Cu and SiO_2. We found that coating leads to decrease of the temperature coefficient of the resistance in measured films. In the whole temperature range, the degradation of the TCR in the Ni films overlayer Cu is more pronounced than in the films overlayer SiO_2. In our opinion, the degradation of the TCR is a result of modification both of the surface and the grain-boundary scattering in Ni films. Decreasing of the value of the coefficient of the specular reflection from the external surface is due to the deterioration of the surface microrelief. Grain-boundary diffusion and absorption of foreign atoms at the grain boundaries results in the degradation of the transparency of the grain boundaries.

Acknowledgements This work was partially supported by the Government Research Program of the Ministry of Ukraine for Education and Science, Reg. No. 0103U000773, 2003-2005. We gratefully acknowledge fruitful discussions with Prof. I.Yu. Protsenko.

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