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CONDUCTION ELECTRON SPIN RESONANCE OF Pt-NANOPARTICLES IN POROUS Al_2O_3 MEMBRANES

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An electron spin resonance (ESR) investigation of Pt-nanoparticles electrodeposited in the channels of porous Al_2O_3 membranes has been performed in the temperature range 6 – 50 K. Pt – particle mean size was evaluated by means of Kawabata theory that relates ESR linewidth to metal particle size. A comparison with the effective crystallite mean size obtained from the X – ray diffraction analysis is given.

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1. Introduction

Anodic porous alumina (Al_2O_3) has recently attracted a great attention as a key material for fabrication of devices on a nanometric scale, such as electronic and photoelectronic devices and for application to micro- and ultrafiltration [1]. Also, nanoelectrode assembly can be obtained by using porous alumina as template.

Porous Al_2O_3 membrane includes numerous cylindrical nanopores (or channels) oriented in paralel to each other and having diameters as small as 11-13 nm [2]. These channels can be filled up with metallic materials by means of electrodeposition method.

Conduction ESR (CESR) spectroscopy is a powerfull tool to study the magnetic behaviour and the electronic structure of small metallic particles [3]. It could also characterize their size according to the theory of Kawabata that relates CESR linewidth to metal particle size [4]. However, reliable experimental verification of this potentially useful theory is lacking and, therefore, a simple measure of small metallic particles size is of considerable significance [5].

To obtain further insight into the physical properties of small metallic particles, an CESR investigation of Pt – nanoparticle electrodeposited in self – assembled channels of porous Al_2O_3 membranes was carried out.

2. Experimental

Small Pt – metallic particles within the channels of Al_2O_3 membranes were produced by an eletrodeposition method at room temperature using H_2PtCl_6 (10 mM) in H_2SO_4 (0.2 M) [6]. The electrodeposition time varied from 20 minutes to 1 hour. The investigated Pt / Al_2O_3 membrane (Pt 1) corresponds to 1 hour deposition time.

X- ray diffraction analysis of porous Pt/Al_2O_3 membrane was done by means of a standard DRON- 3M powder diffractometer.

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ESR measurements were carried out using a Brucker X- band spectometer equiped with a helium gas- flow cryostat.

3. Results and disscusion

The X – ray diffraction pattern of the electrodeposited membranes (Pt 1) is presented in Fig.1. It contains an intense (111) reflection indicating a textured membrane with (111) direction of the Pt type structure. The deposited metal has been confirmed to be Pt (face-centred cubic structure, fcc) with the lattice parameter a_o = 0.392 nm.

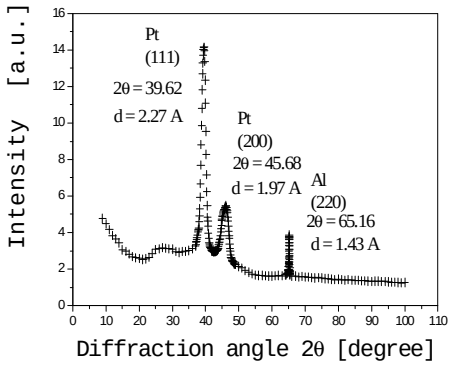

Fig. 1. X – ray diffraction pattern of Pt 1 sample.

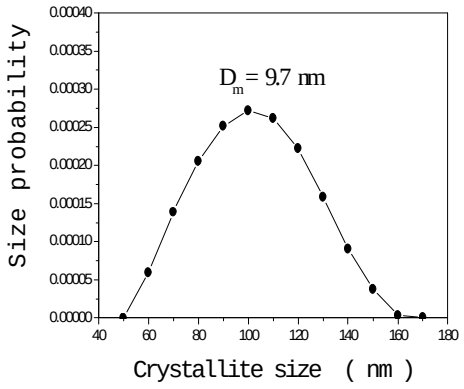

Fig. 2. The crystallite size distribution as a function of the effective crystallite size along the perpendicular direction to the (111) planes (after Aldea and Indrea, 1990).

Fig. 2 shows the crystallite size distribution function as determined from the second derivative of the strain corrected Fourier coefficients [7]. A value of $D_m \approx 9.7$ nm for the Pt – effective crystallite mean size could be evaluated by means of this function.

ESR measurements on Pt/Al_2O_3 membrane show one single line which we assign to an CESR signal of small Pt metallic particles showing quantum size effects. Within the whole temperature range (6 – 50 K) where the resonances were observed, the CESR lines are very asymmetric (Fig. 3). In order to fit the spectra we used an asymmetric Lorentzian function which includes both absorption and dispersion. The fit parameters are the half-width at half-hight, $\delta H_{1/2}$, of the corresponding absorbtion line and the resonance field, H_o.

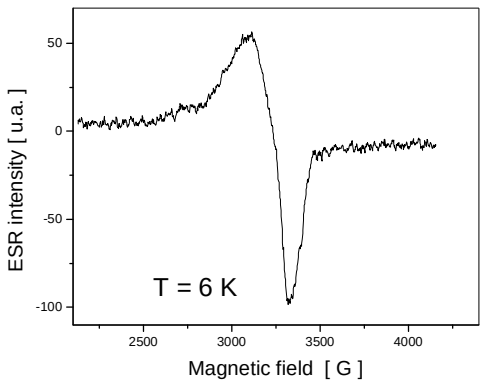

Fig. 3. ESR spectra of Pt/Al_2O_3 membranes.

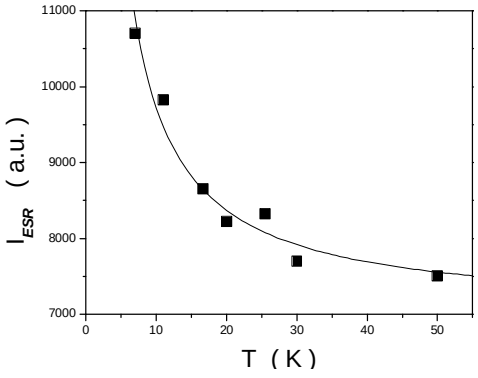

Fig. 4. Temperature dependence of the ESR. The solide line corresponds to the Curie law giving the best fit to the data.

The resulting CESR parameters g = 2.092 and $\delta H_{1/2}$ = 242 Gs are independent of temperature and the asymmetry parameter is e ≈ 0.5. In the investigated temperature range, the integrated ESR intensity, I_{ESR}, displays a Curie behaviour (Fig. 4) in agreement with the theoretical predictions appropiate to quantum size effects of small metal particles [8].

A Curie – like behaviour has previously been reported for ESR in uniform platinum microcrystals having the mean size about 2 nm [9]. The transition from Curie to Pauli behaviour, which is a characteristic feature of the electronic susceptibility in the quantum limit, could unfortunately not be observed since the ESR signal disappears above 60 K.

For the bulk metals the spin relaxation mechanisms is dominated by spin – orbit coupling and the relaxation times are very short. As a result the spectra are too broad to be observed even at low temperatures . When the metal particles are very small, the average electronic energy level spacing, δ, becomes larger than the Zeeman energy $h\nu_e$. In this case the spin relaxation processes are quenched by quantum size effects, resulting in a narrowing of the CESR line [9] .

In accordance with Kawabata's theory, the ESR linewidth of very small metal particles is given by [4].

$$\delta H_{1/2} \cong \frac{V_F (\Delta g)^2 h\upsilon_e}{\delta \gamma_e d_m} \tag{1}$$

where V_F is the Fermi velocity of the conduction electrons, Δg is the bulk metal g shift ($\Delta g = g_{bulk} - g_e$), $h\upsilon_e$ is the Zeeman energy, δ is the average electronic energy level spacing of the metal, γ_e is the electron magnetogyric ratio and d_m is the mean metal particle diameter.

Following Kubo, the quantum size effects alter the electronic properties of small metal particles and we have [8]

$$\delta = \frac{2m_e V_F^2}{3n(\pi/6)d_m^3} \text{ with } \quad V_F = \frac{h}{2\pi m_e}(3\pi^2 n)^{1/3} \tag{2}$$

where n is the number of atoms/m^3 in a particular metal, m_e is the free electron mass and δ is inversely proportional to the particle volume. By combining Eq. (2) with Eq. (1) and using the specific parameters for Pt – metal (ρ = 21.472 g cm^{-3}, M = 195 g mol^{-1}, V_F = 14.4905 m s^{-1}), the expression for $\delta H_{1/2}$ turns out to be [10] .

$$\delta H_{1/2} = 135 \times 10^2 (\Delta g)^2 d_m^2 \ (nm^2)\, G \tag{3}$$

The experimental g – factor of bulk Pt- metal is not known. The corresponding Δg(Pt) could be estimate from the Δg – value for silver metal, Δg(Ag) = -1.9 × 10^{-2} [10]. Because Δg is proportional to λ/ΔE, λ being the spin – orbit coupling, one could consider that the percentage change in Δg is similar to that exhibited by spin orbit coupling in going from Ag(λ = - 1769 cm^{-1}) to Pt(λ = - 2239 cm^{-1}). Then, one gets

$$\Delta g(Pt) = -1.9 \times 10^{-2} \frac{(-2239)}{(-1769)} = -2.4 \times 10^{-2} \tag{4}$$

Substituting into Eq. (3) the evaluated value for Δg (Pt), we estimated the mean diameter of Pt-particles within porous Al_2O_3 channels as $d_m \approx 6$ nm. The observed difference between the Pt–crystallite mean size, D_m, as resulting from X – ray diffraction analysis and d_m evaluated from Kawabata's theory could be partially due to: (i) the uncertainty in Δg (Pt) evaluation (ii) the skin-effect which drives electric and magnetic components out of phase in the sample and therefore Pt – particles large compared to the skin –depth may not contribute to the resonance. The presence of the skin – effect is supported by the asymmetry of CESR line (e > 0) in Pt/Al_2O_3 membrane.

4. Conclusions

The CESR spectra of Pt – nanoparticles deposited in the channels of Al_2O_3 membranes were observed only in a narrow temperature range: 6 - 50 K. The corresponding CESR parameters, g – factor and the linewidth are temperature independent. The ESR integral intensity, which is proportional to the electronic susceptibility, follows a Curie law. It is a characteristic feature of a quantum size effect confirming that the condition $h\nu_e < \delta$ is satisfied for Pt- metal particles.

From the experimental value of the CESR linewidth and taken into account the Kawabata's theory, a Pt- particle mean diameter of ≈ 6 nm was derived. Only a fraction of Pt – particles with the size distribution of Fig. 2 (having diameters less than the skin – depth) is contributing to the resonance.

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