Nanocrystalline cobalt films prepared under ultrafast condensation conditions

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The magnetic and electrical properties and the temperature dependence of these properties of cobalt films prepared at high condensation rates ($10^5 - 10^6$ Å/s) are investigated. Incremented annealing reveals several nonequilibrium states of cobalt in transition from the as-prepared metastable structure to the ordinary hcp structure. The anomalies of the properties are analyzed from the standpoint of the nanocrystalline state of the samples. Model concepts of microcluster formations in the investigated films are also discussed. © *1998 American Institute of Physics.* [S1063-7834(98)02411-3]

Magnetic materials having a nanocrystalline structure are of major interest for several reasons. First, the size of the elementary structural formations (from two to several hundred atoms) is several times smaller than the dimensions of the crystallites in ordinary polycrystalline films. Second, nanocrystalline systems do not constitute a macroscopic system, i.e., the parameters of nanoformations are not a monotonic function of the number of atoms in them. The parameters undergo the most abrupt changes in passage through the so-called ''magic numbers,'' which increases the probability of the generation of nanoformations having a strictly defined number of atoms. The latter feature dramatically increases the accuracy and selectivity of instruments utilizing these materials and thereby expands the area of their practical application. Third, the structure and properties of nanosystems differ from those of solids, and in our opinion their investigation is far from complete.[1–3]

Many properties of microclusters have been studied fairly extensively to date, but the preparation of film materials having a nanocrystalline structure is usually discussed only in the hypothetical realm. On the one hand, the prediction of the properties of such films is highly problematical, because interactions of microclusters with the substrate and with each other begin to play a major role in this case, and these phenomena have received little attention; on the other hand, the technologies used to prepare free-standing microclusters (specifically low-energy cluster beam deposition, or LECBD) are ineffective in film preparation.[4]

The objective of the present study is to investigate the influence of the preparation conditions and the anneal time and temperature on the structure and properties of cobalt films prepared by pulsed plasma deposition (PPD)[5] in a vacuum of $\sim 10^{-6}$ Torr.

1. TECHNOLOGY AND SAMPLES

A distinctive feature of the usable vacuum deposition method is a high pulsed condensation rate (exceeding 10^5 Å/s) at a pulse duration $\sim 10^{-4}$ s with a condensate cooling rate of the order of 10^8 K/s. Inasmuch as a necessary condition for the preparation of nanocrystalline systems is abrupt supercooling of the vapor,[4] our technology is found to be efficient. The technological process essentially entails the production of a plasma between a water-cooled anode and a sputtered target of pure cobalt by discharging a high-capacitance bank of capacitors in the vapor of the sputtered target. An initial small quantity of vapor is created by preliminary laser evaporation of the target. In the main stage of the process an LTI-207 solid-state laser partially evaporates the cathode to create a medium for the passage of an electric current. Each evaporated atom is ionized in the discharge plasma, i.e., generates one electron and one ion. The resulting target atoms bombard the material to be evaporated, knocking out a new batch of atoms. The sputtering process continues for a period exceeding the duration of the laser pulse by three or four orders of magnitude.

The method is novel in that one can select the direction of maximum dispersion of the crystal structure at ultrahigh condensation rates, when the number of new nucleation centers is so large that the radius of the critical nucleation center is the same as the radius of coalescence.[5] Films prepared by this method are continuous, beginning with a thickness of $10 - 15$ Å, and comprise a set of nanocrystallites of approximately equal diameter. These data have been established from electrical resistivity measurements and from measurements in high-resolution tunneling and transmission electron microscopes. The electron diffraction pattern appears as a diffuse halo typical of amorphous and nanocrystalline materials.

2. EXPERIMENTAL RESULTS

The electrical and magnetic properties of the prepared samples have been subjected to temperature analyses. Figure 1 shows the thickness dependence of the electrical resistivity $\rho(d)$ of a cobalt film obtained during deposition. Three distinct intervals are visible on this curve. In the first interval (to a thickness $d_1 \lesssim 15$ Å) we observed a sharp decrease in ρ due to the transition from an island structure to a continuous film. This behavior of the curve confirms the continuity of the film
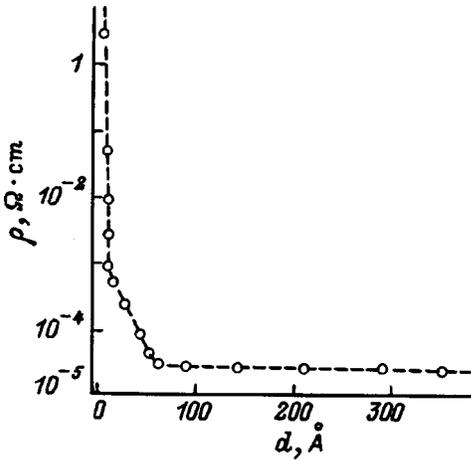
FIG. 1. Electrical resistivity versus thickness of a Co film.

TABLE I. Dependence of the ratio of the electrical resistivities at room temperature and liquid-nitrogen temperature on the thickness of a Co film.

Film thickness, Å	$\rho_{300\,K}/\rho_{77\,K}$
70.	1.01
120.	1.015
300.	1.03

beginning with a monolayer consisting of nanocrystallites. In the second interval (ranging from 15 Å to 60 Å) we observe a somewhat different kind of behavior, which can be identified with the dependence of the effective mean free path of electrons on the sample thickness, i.e., the relation $d < L_q$ (where L_q is the mean free path) holds in the given thickness range. Finally, in the third interval (>60 Å) ρ is essentially independent of d. The value of L_q can be roughly estimated from this dependence and for the given sample is $\sim 60 - 70$ Å.

Preliminary studies have also shown that in the initial state the temperature coefficient of the resistance (TCR) of the samples is close to zero, and their resistivity ρ is high, exceeding by more than an order of magnitude the value of ρ for ordinary polycrystalline cobalt films.

Figure 2a shows the characteristic temperature dependence of the resistivity $R(T_n)$. A Co film of thickness $d = 750$ Å, deposited on glass-ceramic, was used in the given situation. The temperature curve exhibits a complex behavior. During initial heating, we observe a slight increase in R up to a temperature ~ 450 K and then, as T_n increases, two rather sudden drops in the resistivity, which are separated by a short temperature interval (520–600 K) wherein R stabilizes. The resistivity drops differ for different films, but are essentially independent of the initiation temperature and, as a
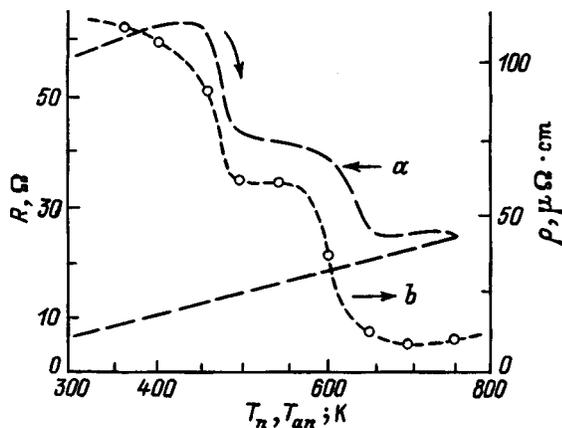
rule, cease at $T_n \sim 670 - 675$ K. The opposite behavior of the $R(T_n)$ is characteristic of metals, i.e., is linear. The total resistivity drops by a factor of 1/5 to 1/15, depending on the sample thickness, and is irreversible.

It is natural to assume that this behavior is associated with temperature-induced transformation of the nonequilibrium structure of the samples. The influence of temperature on the resistivity was subsequently determined by a series of anneals. A large number of films was subjected to incremented annealing at various temperatures (T_{an}) in the range from 350 K to 850 K in a vacuum of 10^{-5} Torr. The anneal time at each fixed temperature was 1 h. Figure 2b shows the resistivity of a Co film deposited on a glass substrate as a function of the anneal temperature. It is evident from this figure that in the as-prepared state ρ is more than 20 times the resistivity of bulk Co and decreases by almost one half at $T_{an} = 450$ K. With a further increase in T_{an} in the temperature interval $500 - 650$ K ρ decreases to $\cong 12\ \mu\Omega \cdot$cm. This value is characteristic of polycrystalline cobalt films.

The TCR has also been investigated on Co films in the temperature range 300–77 K. The results are summarized in Table I. These data show that the resistivity depends weakly on the thickness and temperature over a wide range of thicknesses. Control measurements to helium temperatures give the same values of the TRC. These experiments indicate that the character of the carriers does not change and that the variation of the resistance is associated with structural transformation.

The temperature dependence of the magnetization (I_s) and the coercive force has also been investigated. In the as-prepared state the films are magnetic, with the magnetization measured at $T = 300$ K — approximately 800 G, which is much lower than the magnetization of bulk Co. The degree of stability of this equilibrium state of cobalt could be determined from temperature analyses during both the preparation and the annealing of the films.

Figure 3 shows the results of such measurements for films prepared at various temperatures and on various substrates. The substrates were changed to test the influence of their crystalline nature on the magnetic state of the prepared films. It is evident from Fig. 3 that films obtained at room temperature are magnetic, but their magnetization is much lower than that of pure cobalt. An increase in the substrate heating temperature during preparation lowered the value of I_s on glass substrates, caused it to vanish altogether on MgO substrates, and reduced it almost to zero on mica substrates. Raising the substrate temperature above 500 K increased the saturation magnetization, and at $T_n \geqslant 570$ K the magnetization of the films corresponded to the value of I_s for bulk polycrystalline cobalt. The very complex behavior of the

FIG. 2. Variations of the electrical resistance R during heating (a) and the electrical resistivity ρ during annealing (b).
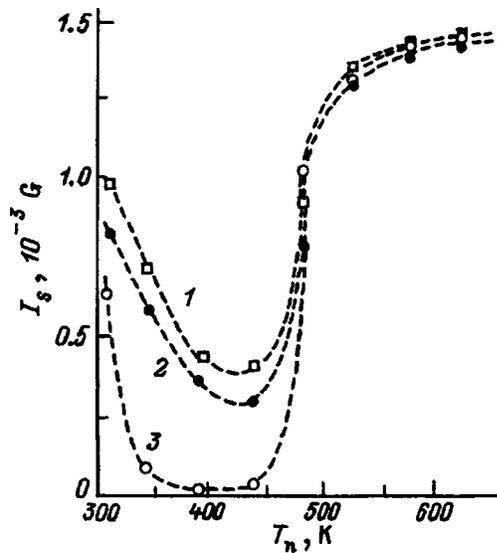
FIG. 3. Influence of substrate temperature during preparation on the magnetization I_s of cobalt films deposited on various substrates: *1*) glass; *2*) MgO single crystals; *3*) mica.

magnetization is evidence of complex structural transformations in the samples under the influence of temperature.

Anomalies in the behavior of the saturation magnetization as the substrate heating temperature is varied during film preparation have been determined from an analysis of the curve representing I_s as a function of the anneal temperature for a specially selected sample of nonequilibrium cobalt. The film in the as-prepared state had a magnetization of 850 G, which is much lower in absolute value than the magnetization of bulk Co. The film was annealed incrementally in 50-K steps for one hour at each fixed temperature in a vacuum of 10^{-5} Torr. The results of the experiment are shown in Fig. 4. It is evident from this figure that I_s decreases almost to zero as T_{an} is increased approximately to 500 K. A further increase in the temperature causes the magnetization to increase almost to the characteristic value for bulk Co (1460 K).

An analysis of the measurements of the magnetic properties has shown that a Co film prepared in the presence of ultrafast condensation has a minimum of three different states, depending on the degree of influence of the tempera-
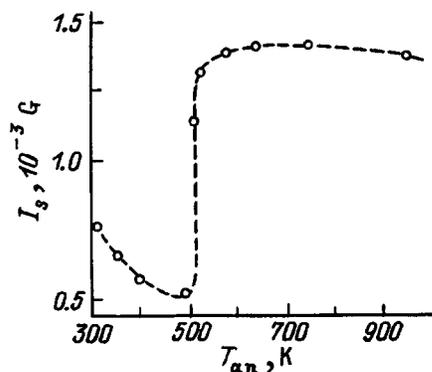

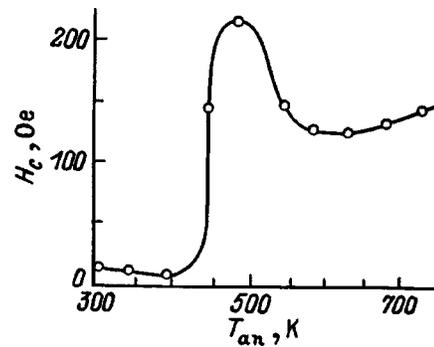FIG. 4. Influence of high-temperature annealing on the saturation magnetization of a Co film.

FIG. 5. Influence of high-temperature annealing on the coercive force of a Co film prepared by pulsed plasma deposition on a glass substrate at room temperature.

ture both as the condensate is formed during growth and as it is modified during annealing: 1) The film is ferromagnetic, but the saturation magnetization is approximately one third the value in bulk samples; 2) the magnetization of the film is lower than in the first state or is even close to zero; 3) the film has the magnetization of bulk cobalt.

The coercive force of the investigated films also exhibits a strong temperature dependence. It is evident from Fig. 5 that the variations of H_c take place in the same temperature intervals as in the case of ρ and I_s.

3. DISCUSSION OF THE RESULTS

The reported experimental measurements of the magnetic and electrical properties demonstrate their extraordinary behavior both in the as-prepared state and under the influence of temperature. On the whole, the anomalies of both the magnetic and the electrical properties are associated with the same temperature intervals, and the facts of their temperature dependence and irreversibility attest to structural phase transformations. As shown above, in the as-prepared state the structure is associated with the ultradisperse state and comprises a set of microclusters having a diameter of 20–30 Å. The electron diffraction patterns recorded from samples in the as-prepared state show a diffuse halo typical of the amorphous or ultradisperse state (Fig. 6a). Consequently, the sum-total of our structural measurements along with the measured magnetic and electrical properties show that the as-prepared films exist in a nonequilibrium state and have a microcluster structure.

The current literature contains abundant descriptions of preparation techniques the properties of microclusters of 3*d* metals as well as films having a microcluster structure.[6–8] More often than not cluster technology is largely associated with the application of cluster beams, which are the simplest to create in the case of a freely flowing gas or vapor by sputtering in vacuum. In this case the cluster emerges as an intermediate phase between the gaseous and condensed states. Clusters are efficiently generated under nonequilibrium conditions by converting the gas or vapor into clusters. All cluster generation methods are based on vapor formation, i.e., they utilize the phenomenon of cluster formation from supersaturated vapor as a result of its expansion in a low-pressure region (vacuum). The cooling of the vapor-plasma
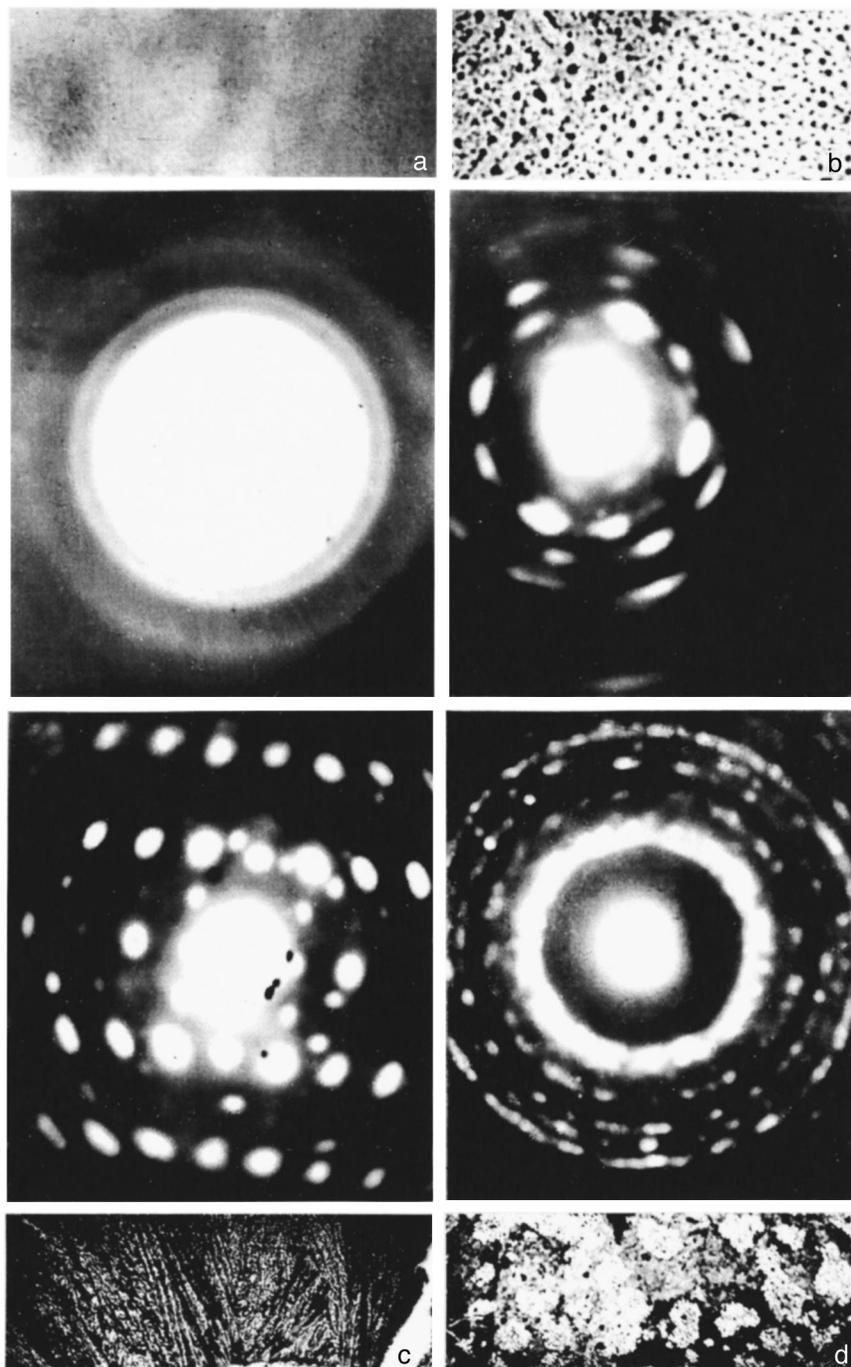
FIG. 6. Results of electron microscope analysis of Co films subjected to various heat treatments. a) Film as prepared at room temperature; b–d) after anneals at: b) 400 K; c) 480 K; d) 650 K. Magnification in the photomicrograph fragments: ×20 000.

mixture during expansion leads to the formation of clusters. Consequently, the most efficient method for the generation of cluster beams is laser evaporation, owing to the high specific surface temperature involved.[4]

The sample preparation technology used by us mainly has the same attributes as those described in the literature and used extensively for the production of cluster beams. However, when films prepared by these technologies are built up from low-energy cluster beams (neutral or unaccelerated), they are similar to ordinary films grown by thermal evaporation. In this case, since the beam has low energy (less than 1 eV/atom), a cluster sticks to the grown film, and its atoms spread out over the surface.[4] In our case a high-energy

efficiency of the vapor-plasma mixture is maintained by an applied electric field of 500 V.

Microclusters (including those in films) are preserved if they are separated or exist in a special closed state (as in the case of fullerenes or fullerenelike formations). Since a high specific surface and high reactivity are distinguishing features of clusters, microclusters can be contained in a shell of carbon or nitrogen atoms inherent in a residual vacuum atmosphere.

To test this hypothesis, we have used Auger electron spectroscopy to analyze the chemical composition of cobalt films prepared by PPD. Figure 7 shows the Auger profile of the depthwise distribution of elements in the sample. The
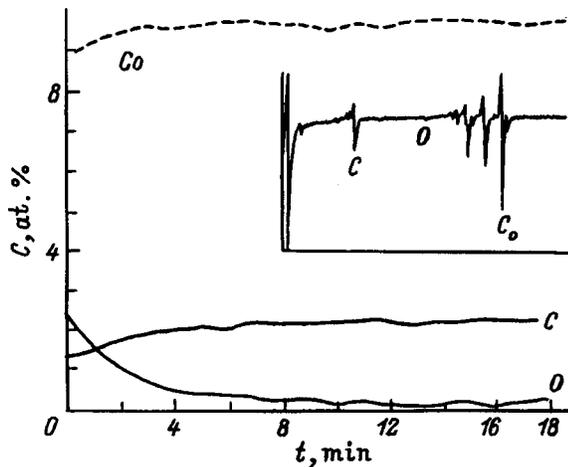
FIG. 7. Auger spectrum of the distribution of elements along the depth of a sample. Inset: panoramic spectrum of the film surface after layer-profiling analysis.

results of estimating the element concentrations with allowance for the element sensitivity factors are shown in Table II. The data in the second row of the table have been obtained for a sample previously etched with an Ar^+ ion beam to the entire measurement depth.

The results of this investigation reveal an extraordinarily high carbon content (more than 30 at. %) in the film. In conventional thermal methods of film preparation in a vacuum of the order of 10^{-6} Torr the carbon content does not exceed 3–4 at. %, and the oxygen content is approximately four times higher than in our case. Such a high C content is clearly associated with the specifics of the PPD method. We can assume that carbon ions are trapped both during the transit time of atoms of the deposited material to the substrate by virtue of the high degree of ionization of the vapor and also during condensate formation as a result of the long spacing between deposition pulses.

Proceeding from the sum-total of data on the magnetic and electrical properties and from structural and spectral measurements, we can assume that the resulting condensate comprises cobalt clusters surrounded by a kind of carbon ''overcoat.'' A substantial transformation of the electron structure can be expected in such structural formations, conducive to variations of the magnetization and other properties.

Figure 6 shows electron diffraction patterns with insets of fragments of photomicrographs of cobalt films subjected to various degrees of heat treatment. Figure 6a shows an electron diffraction pattern of the original film as prepared without preheating of the substrate. The film is x-ray amor-

phous. Heating to 400 K already produces reflections of the newly formed phase against the background of halo rings (Fig. 6b). It is important to note that the positions of these reflections is confined to the width of the halo rings. Annealing at a temperature of 450–475 K produces a specific electron diffraction pattern of single-crystal reflections (Fig. 6c). The displayed diffraction pattern is one of three typical patterns obtained with dendrites of different configurations and crystallographic orientations. A series of such diffraction patterns has enabled us to calculate the possible structural type of the microclusters. The microstructure of the films is a network of dendrites (Fig. 6c) growing out from the crystallization centers.[9] The crystallization itself exhibits all the signs of an explosive process. Finally, after annealing at 600–650 K the electron diffraction pattern has a series of rings typical of hcp Co. The photomicrograph in this case shows that the nonequilibrium dendritic structure has disintegrated, and the film is now becoming polycrystalline (Fig. 6d).

In several earlier papers we have already investigated the possible structural type of newly formed microclusters.[9–11] A film in the as-prepared state consists of a highly disordered system of microclusters classified as one of the stable nanostructures. It has been substantiated theoretically and experimentally that the most stable structures in the range of dimensions $\leqslant 30$ Å are the octahedron and the cuboctahedron. The rigorous description of the stable structure of certain metal clusters yields the well-known jellium model, or shell model,[3] where metal clusters are regarded as giant macroatoms with electron energy levels that exhibit a shell structure. Because of its high reactivity, such a system can in orderly fashion incorporate carbon atoms, which can reside inside the cluster and also form outer shells. Corroboration for this kind of model can be found in the high carbon concentration actually encountered in our films and in data on the structure of capsulated $3d$ metals.[6,7]

If we assume that the octahedron is the smallest block in a cuboctahedron and take account of the fact that some of the carbon atoms in the system form a carbide configuration, we can then understand the reduced magnetization, high resistivity, zero TCR, and other physical properties of Co films. The initial anneal leads to structural quasiordering of the initially disordered system of microclusters. The possible type of crystallization is the previously observed[12,13] and theoretically calculated ''quasimelting'' mechanism, when the structural blocks, or microclusters, ostensibly rotate about one another under the influence of not too high temperatures of 450–470 K, forming long, drawn-out dendrites. This process occurs within short time periods and resembles explosive crystallization. ''Building blocks'' (microclusters) of these dendrites are genetically assimilated into the initial condensates. This ordering process promotes a further reduction in the magnetization and in some cases causes it to disappear altogether (Fig. 3), and at the same time it has the effect of almost doubling the electrical conductivity (Figs. 2a and 2b).

After high-temperature (above 550–600 K) annealing the film structure relaxes to equilibrium, accompanied by disintegration of the microcluster system, and the saturation

TABLE II. Element concentrations, calculated with allowance for the element sensitivity factor, on the as-prepared surface and after Ar^+ ion-beam etching to a depth of 150 Å.

Surface	S	Cl	Ar	C	N	O	Co	Na
As-prepared	0.004	0.023	–	0.235	–	0.316	0.422	–
After Ar^+ etch	–	–	0.005	0.304	–	0.009	0.680	–

magnetization increases to the value inherent in bulk cobalt. Now the film also exhibits all the electrical properties similar to those of a polycrystalline cobalt film.

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