

The Effect of Substrate Temperature on the Structure and Magnetic Properties of Cobalt Films Deposited by CVD

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Abstract. In this work the effect of substrate temperature on the structural parameters (sizes of coherent scattering region, values of microstresses), phase and chemical composition, surface morphology of Co films is revealed. Moreover, the correlation between structure, cobalt content and magnetic, electrical characteristics of Co films is presented. Co films were deposited on Si (100) substrates by chemical vapor deposition using the diiminate complex $\text{Co}(\text{N}^i\text{acN}^i\text{ac})_2$ as a precursor. The sizes of coherent scattering region, values of microstresses and phase composition of Co films were determined by the X-ray diffraction analysis. The chemical composition was identified by the Energy-dispersive X-ray spectroscopy. The surface morphology of Co films was investigated by atomic-force microscope. Magnetic characteristics were measured by vibromagnetometer and the electrical resistivity was measured by four-probe dc method. It is found that the variation of deposition conditions allows widely changing structural parameters and chemical composition of Co films.

1. Introduction

Thin films of cobalt have been the subject of significant scientific research and have attracted great interest with respect to applications in composite magnets for micromechanics, data storage devices and sensors [1, 2].

There are currently many deposition techniques for metal films. However, chemical vapor deposition (CVD) has a special place among them. CVD is a technique which offers potential for producing films with high uniformity of thickness and composition, high purity, minimal substrate damage, high deposition rates and the possibility for selected area growth [3]. Moreover, CVD allows obtaining thin films with a different structure (different size and shape of the grains, texture) and effectively varying the thickness, phase and chemical composition of films in a wide range during their growth [4].

Properties of the films obtained by CVD, essentially depend on the deposition parameters (substrate temperature, vaporization temperature, duration of deposition process). The effect of CVD-deposition conditions on the properties of Co films has already been studied [5]. Nevertheless, very little empirical research has been carried out to investigate Co films deposited by CVD where a precursor was the diiminate complex $\text{Co}(\text{N}^i\text{acN}^i\text{ac})_2$ that was characterized by a good volatility and high stability [6].

Therefore, to obtain films of Co with the specified operational characteristics by CVD using the diiminate complex as a precursor it is necessary to reveal the dependence of structure, phase and



chemical composition on deposition conditions. The aim of this research is to investigate the effect of substrate temperature on the structural parameters (sizes of coherent scattering region, values of microstresses), phase and chemical composition, surface morphology of Co thin films deposited by CVD. Furthermore, the correlation between structure, cobalt content and magnetic, electrical characteristics of Co films is presented in this work. It is expected that the variation of deposition conditions allows widely changing structural parameters and chemical composition of Co films.

2. Experimental details

Co films were deposited on Si (100) substrates by CVD. $\text{Co}(\text{N}'\text{acN}'\text{ac})_2$ was used as a precursor. The deposition conditions were as follows: gas-carrier flow rate (Ar) was 1 l/h, gas reagent flow rate (H_2) - 4 l/h, the operating pressure was atmospheric (~ 760 Torr), the deposition process was carried out during a period of 4h. The vaporization temperature (T_{vap}) was fixed and was equal to 130 °C, while the substrate temperatures (T_s) were varied in the range from 300 to 340 °C.

The X-ray diffraction (XRD) analysis of the samples was performed on a DRON-SEIFERT-RM4 diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.54051$ Å). The chemical composition was identified by the Energy-dispersive X-ray spectroscopy. The surface morphology of Co films was investigated by atomic-force microscope (AFM) Solver HV. Magnetic characteristics were measured by vibromagnetometer VM-23K in the easy direction of magnetization. The electrical resistivity was measured by four-probe dc method. All measurements were carried out at an atmospheric pressure and at room temperature.

3. Results and discussion

According to XRD data, the most intensive diffraction peak centered at around $44,2 - 44,7^\circ$ in 2θ is observed in the samples deposited at substrate temperatures $T_s = 300\text{--}340^\circ\text{C}$ (figure 1). Detailed analysis of XRD pattern reveals that this diffraction peak is positioned between (111) of β -Co (face centered cubic) at $44,3^\circ$ and the (002) reflection of α -Co (hexagonal close-packed) at $44,6^\circ$.

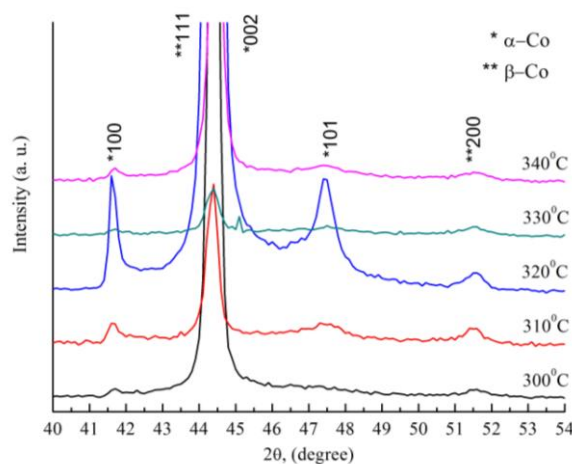


Figure 1. XRD patterns of the Co films deposited at different substrate temperatures.

Moreover, the XRD pattern for Co samples deposited at $T_s = 300 - 340^\circ\text{C}$ contains additional peaks, which could be indexed to the α -Co (100) ($2\theta = 41.7^\circ$), α -Co (101) ($2\theta = 47.6^\circ$) and β -Co (200) ($2\theta = 51.7^\circ$) (figure 1). The height of the diffraction peaks is governed by the substrate temperature. The XRD peak becomes higher with increasing substrate temperature from $T_s = 300$ to $T_s = 320^\circ\text{C}$. However, further growth of substrate temperature up to $T_s = 330$ and 340°C results in a gradual weakening of the peaks. The Co film deposited at substrate temperature $T_s = 320^\circ\text{C}$ is noted to be characterized by well-pronounced texture (the maximum height of the diffraction peaks).

The sizes of the coherent scattering region (CSR), microstress values and chemical composition of Co films under study are presented in table 1. As seen from the table 1, the CSR size of films weakly depends on the substrate temperature in the range of temperatures from 300 to 330 °C. However the CSR size starts to decrease after increasing temperature over 330 °C.

It should be noted that substrate temperature does not affect microstresses of Co films. Values of microstresses are kept constant within the measurement error (table 1).

As listed in the table 1, there are atoms of carbon, oxygen and nitrogen in Co films. The Energy-dispersive X-ray spectroscopy demonstrates that the chemical composition of Co films is characterized by the extreme dependence on the substrate temperature. Actually, the increase in the substrate temperature from 300 to 330 °C on the one hand is accompanied by a growth of the cobalt content from 84.8 to 93.5 at. % and on the other hand leads to a decline in the carbon content from 14.2 to 6 at. %. However, further rise in substrate temperature up to 340 °C causes both a decrease in the cobalt content down to 90.9 at. % and an increase in the carbon content up to 8.8 at. %.

Table 1. Chemical composition, CSR size, microstresses σ and electrical resistivity ρ of Co films deposited at different substrate T_s temperatures.

T_s (°C)	Chemical composition	CSR (nm)	σ (GPa)	ρ ($\mu\Omega\cdot m$)
300	Co 84.8%, C 14.2%, O 0.1%, N 0.9%	35	0,4	0,36
310	Co 86.5%, C 12. 6%, O 0.2%, N	26	0,5	0,34
320	Co 92.3%, C 7. 2%, O 0.5%	33	0,2	0,12
330	Co 93.5%, C 6.0%, O 0.5%	26	0,4	0,07
340	Co 90.9%, C 8.8%, O 0.3%	20	0,3	0,1

According to AFM investigations, Co films deposited at substrate temperature $T_s = 300 - 330$ °C are characterized by fine – grained surface relief (figure 2, a-d). However, further growth of temperature up to $T_s = 340$ °C leads to a disappearance of the film's grain structure. As seen in figure 2, e, the presence of grain structure is less apparent.

Structural parameters and chemical composition determine magnetic and electrical properties of Co films. A comparison of hysteresis loops of films deposited at different substrate temperatures indicates that the Co films, obtained at $T_s = 330$ °C, are characterized by higher residual magnetization and saturation magnetization compared to films deposited at 300 °C (figure 3, a, c). The latter is associated with an increase in cobalt content in films deposited at higher substrate temperatures (table 1). The electrical resistivity of Co films is also governed by the content of cobalt. Indeed, films deposited at $T_s = 330$ °C, are characterized by the maximum cobalt content (93.5%), and hence the minimum electrical resistivity (0.07 $\mu\Omega\cdot m$) (table 1). In contrast, the coercive force of Co films mainly depends on their degree of texture. Films, deposited at $T_s = 320$ °C, are characterized by higher value of the coercive force because these films were most textured (figure 3, b and figure 1).

4. Conclusion

The results of the performed investigations show that Co films deposited by chemical vapor deposition consist of α -Co and β -Co crystals. Varying the substrate and vaporization temperatures allows us to modify widely the microstructure and chemical composition of Co films. A rise in substrate temperature causes a decline in sizes of the coherent scattering region and results in the disappearance of the grain structure of Co films. The cobalt content and texture of films are characterized by the extreme dependence on the substrate temperature with a maximum at 320-330 °C. However, microstresses of films don't depend on substrate temperature and remain unchanged.

The selection of the optimal combination of deposition parameters allows obtaining films of cobalt with required magnetic and electrical properties. The residual magnetization and saturation

magnetization of films rise and the electrical resistivity decreases with increasing cobalt content. An increasing the degree of texture of Co films raises their coercive force.

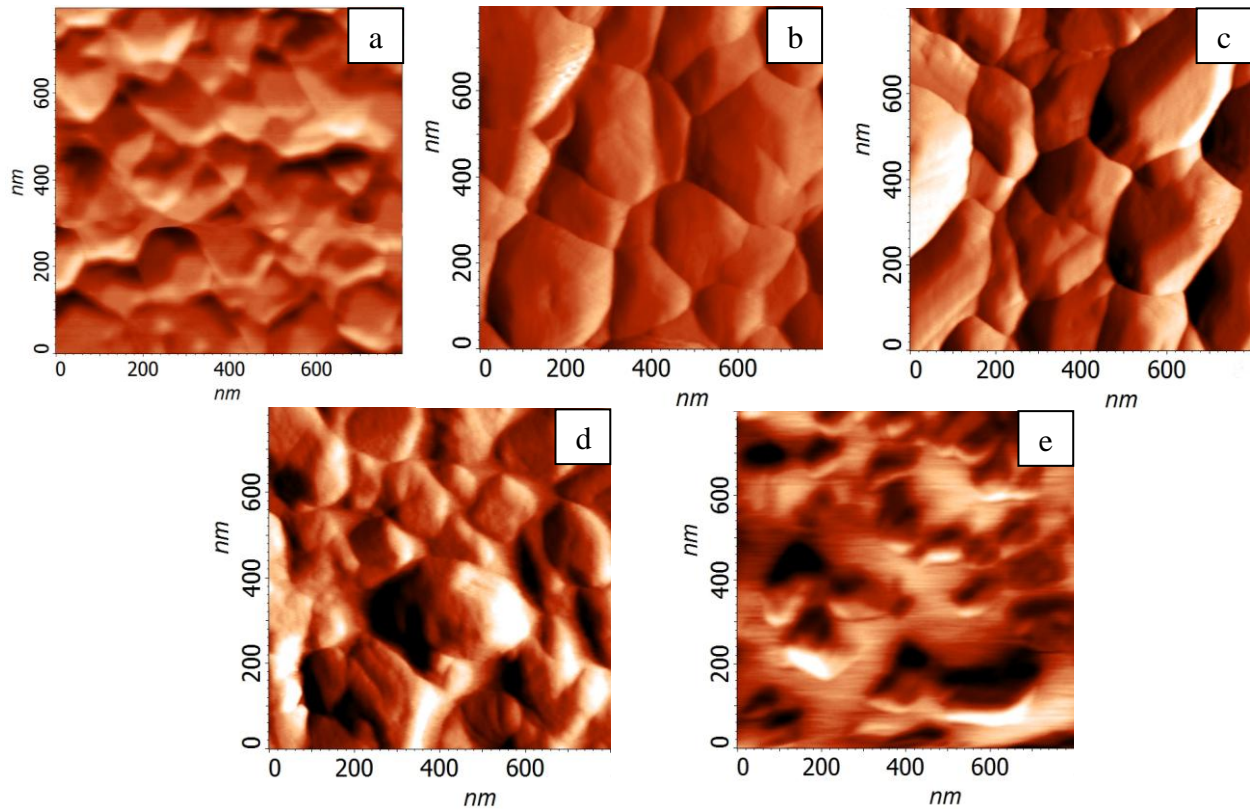


Figure 2. AFM-images of the Co films deposited at $T_{\text{vap}}=130$ °C and $T_s = 300$ (a), 310 (b), 320 (c), 330 (d) and 340 °C (e).

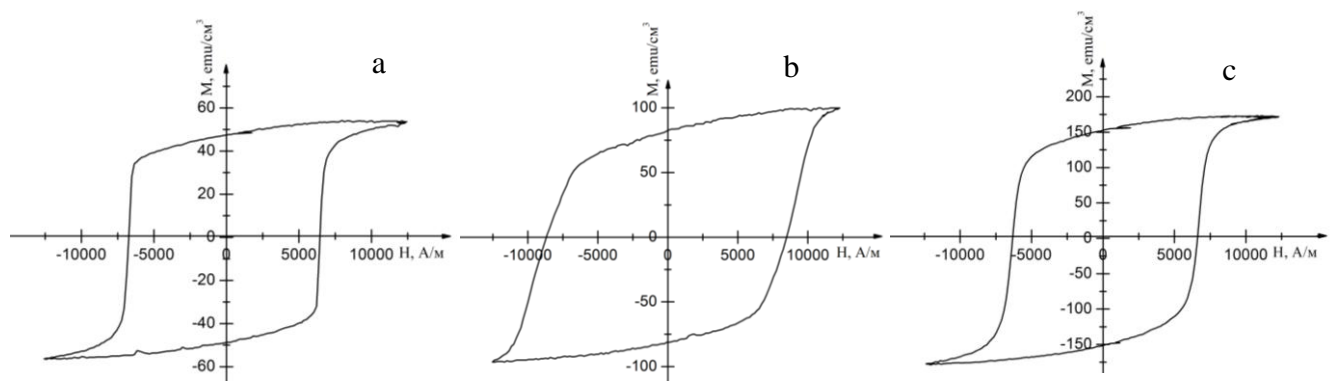


Figure 3. Hysteresis loops of the Co films deposited at $T_{\text{vap}}=130$ °C and $T_s = 300$ (a), 320 (b) and 330 °C (c).

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