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V.A. Chernov, N.I. Chkhalo, M.V. Fedorchenko,
E.P. Kruglyakov, S.V. Mytnichenko, S.G. Nikitenko

EXAFS, PXRD AND SAXS STUDIES OF ANNEALING IN Co/C AND Ni/C MULTILAYERS MANUFACTURED BY PULSED LASER EVAPORATION METHOD

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НОВОСИБИРСК

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V.A.Chernov, N.I.Chkhalo, M.V.Fedorchenko, E.P.Kruglyakov, S.V.Mytnichenko, S.G.Nikitenko

Siberian SR Centre at Budker Institute of Nuclear Physics, Lavrentyev Avenue 11, Novosibirsk, 630090, Russia
Telex: 133116 ATOM SU. Fax: (3832) 35−21−63

Abstract

A detailed study of structural changes occurring in films and on boundaries in multilayers at annealing with EXAFS, PXRD and SAXS methods was performed. The optimum temperature of annealing for the Ni/C and Co/C multilayers obtained by the pulsed laser evaporation method was found.

1. Introduction

The temperature dependence of the multilayer structure (MLS) properties is of interest for two main reasons. First, heating of the mirrors is probable in real experiments (powerful synchrotron radiation, high temperature plasma). The second reason is the stabilization and even the improvement of x−ray optical parameters. Such a possibility was first indicated by Barbee [1] for W/C MLS. In Ref. [2] the number of Me/C type structures studied (Me= WRe, Co, Cr, W) was expanded. In later studies [3] the assumption was suggested on the structural changes in metal films starting from annealing temperature ~470 K. In Ref. [4] the period variation of multilayer mirrors before and after annealing was referred to variations in carbon film density. In Ref. [5] the conclusion was made that all the features of temperature behaviour of MLS properties cannot be explained only by the density variation of carbon film and more complex processes should be taken into account.

One should mention that all these data were obtained for the structures prepared with the sputtering and thermal evaporation methods which have the lower value of the intermediate layer compared to that in the pulsed laser evaporation (PLE) method. The presence of a substantial intermediate layer [6] can change strongly the temperature characteristics of the multilayer.

The present work is performed aiming at detailed study of structural changes occurring in films and on boundaries in multilayers at annealing and also the defining of optimum annealing temperature for the "classical" Ni/C and Co/C multilayers obtained by the PLE method.

A detailed description of multilayer deposition conditions, measurements of their geometric parameters, possibilities of the used apparatus for the study one can find in Ref. [6].

2. Annealing treatment

A study of thermal annealing was performed on four samples whose parameters are given in Table 1. The MLS temperature dependence was taken within the range from 490 to 710 K. The upper temperature was limited by the degradation of structures. The MLS samples were annealed for 1.5 h in a furnace at a 10^{-6} Torr pressure. After each successive treatment and prior to performing measurements the samples were cooled down to room temperature.

Table 1. Geometric parameters of studied samples: N -number of periods, d-period, h_m, h_c-thickness metal and carbon layers, σ -roughness.

Sample Number	Materials	N	d, Å	h_m, Å	h_c, Å	σ, Å
1	Ni/C	30	43.7	13.0	30.7	2.5
2	Ni/C	33	43.1	24.7	18.4	4.4
3	Co/C	35	39.1	21.6	17.5	3.5
4	Co/C	31	43.4	12.4	31.0	2.5

3. SAXS measurements

Small-angle x-ray scattering (SAXS) measurements were performed on a conventional θ/2θ diffractometer in the region spanning the total reflection regime and the first Bragg peaks resulting from modulated superstructure. The detailed description of SAXS measurements will be given in Ref. [6].

Fig.1 shows angular dependencies of reflection coefficients of x-ray radiation with wavelength 1.54 Å (Cuk_α line) from the sample 1 at various annealing temperatures. Fig.2 shows the first Bragg peak reflectance versus annealing temperature for all studied samples. In Fig.3, we have plotted versus temperature the relative variation of period Δd/d compared to the initial period of samples 1,2,3. Fig.4 shows the interface roughness versus annealing temperature.

This study revealed following regularities.

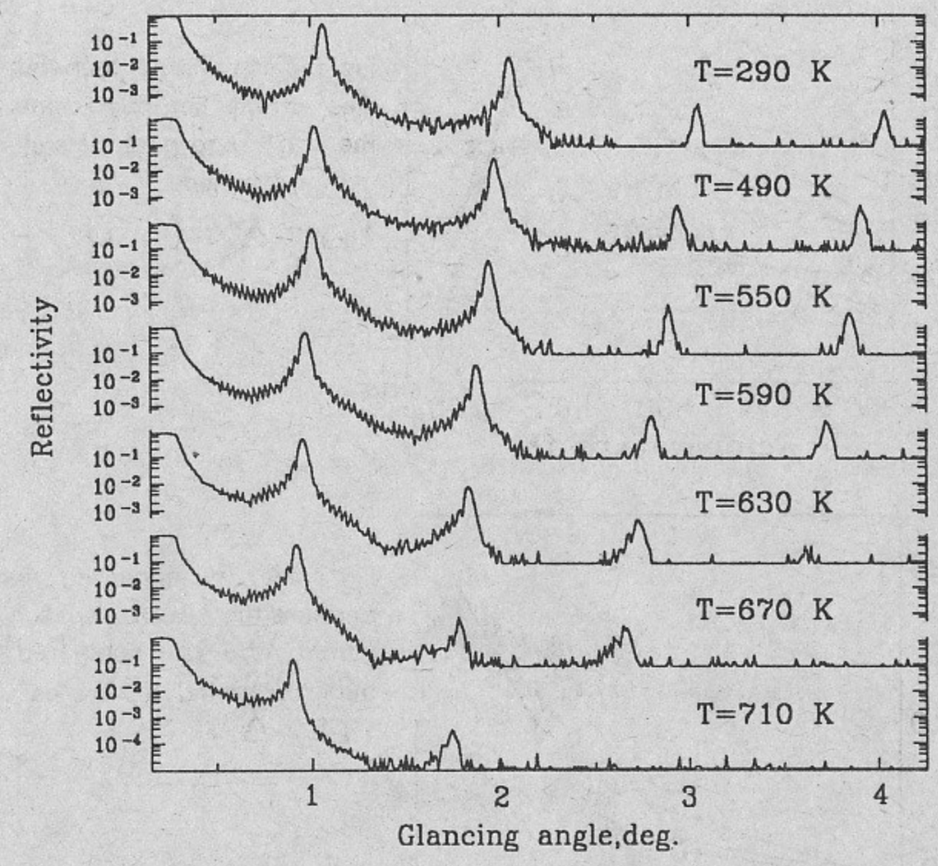

Fig.1 Angular dependencies of reflection coefficients of x-ray radiation with a wavelength λ=1.54 Å ($Cu_{K\alpha}$ line) from the first sample at various annealing temperatures.

A substantial growth of the reflection coefficients in the 1st Bragg's peak up to the annealing temperature 620 K and then its sharp decrease because of the growth of roughness are observed.

The MLS periods increase with temperature up to 670 K. The relative change of the period Δd/d~18 % at 670 K was found. It is substantially larger than change in the period at annealing of MLS deposited by the traditional methods [5] (Δd/d~13 % under the same conditions). This difference can be explained as well by the large depth of the intermediate layer [6] as by the large density of carbon (2.6 g/cm^3) evaporated with pulsed laser evaporation method compared to those obtained with conventional methods.

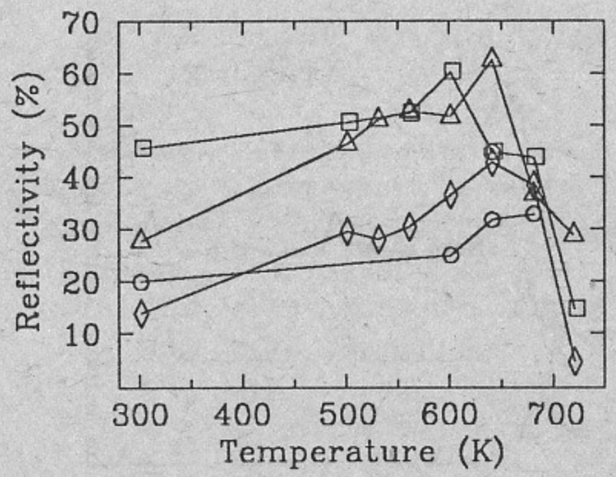

Fig.2 Temperature dependencies of reflection coefficients in the first Bragg peak at annealing for samples:
1-□, 2-△, 3-◊, 4-○.

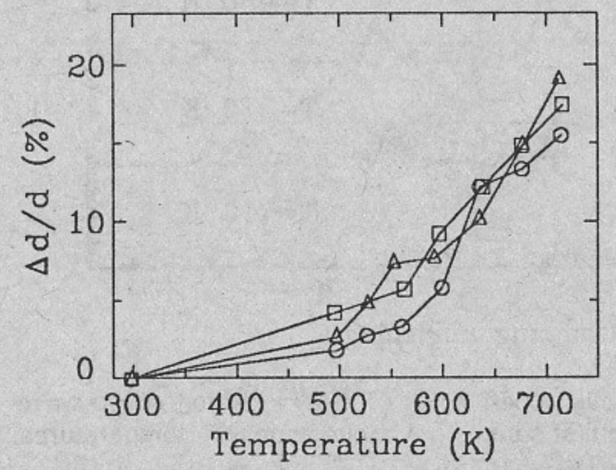

Fig.3 Versus annealing temperature the relative variation of period Δd/d (%) compared to the initial period of samples:
1-□, 2-△, 3-○.

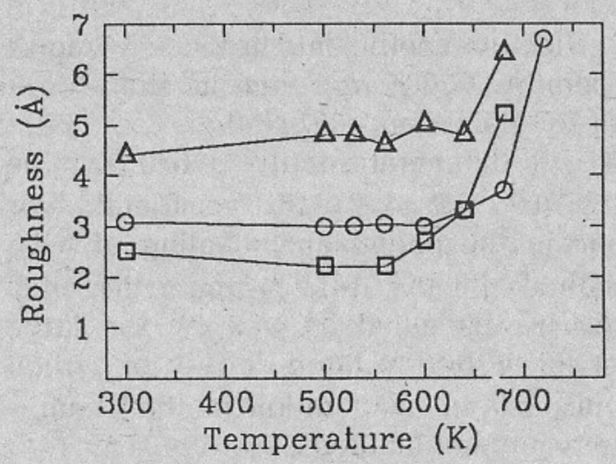

Fig.4 The interface roughness σ (Å) versus annealing temperature for samples:
1-□, 2-△, 3-○.

4. PXRD study

Experiments on PXRD (powder x−ray diffraction) have been carried out on "Anomalous scattering" (primary monochromator Si (111), secondary − LiF (200), λ=1.53 Å) and "Diffraction Cinema" (focusing monochromator − Ge (111), the position sensitive detector OD−2, λ=1.53 Å) stations at the VEPP−3 storage ring of the INP at Novosibirsk [7].

Fig.5 shows the diffraction patterns obtained for sample 2 during the annealing. Up to the 630 K nickel in the whole remains in amorphous state, certain state of crystallization takes place. Annealing at

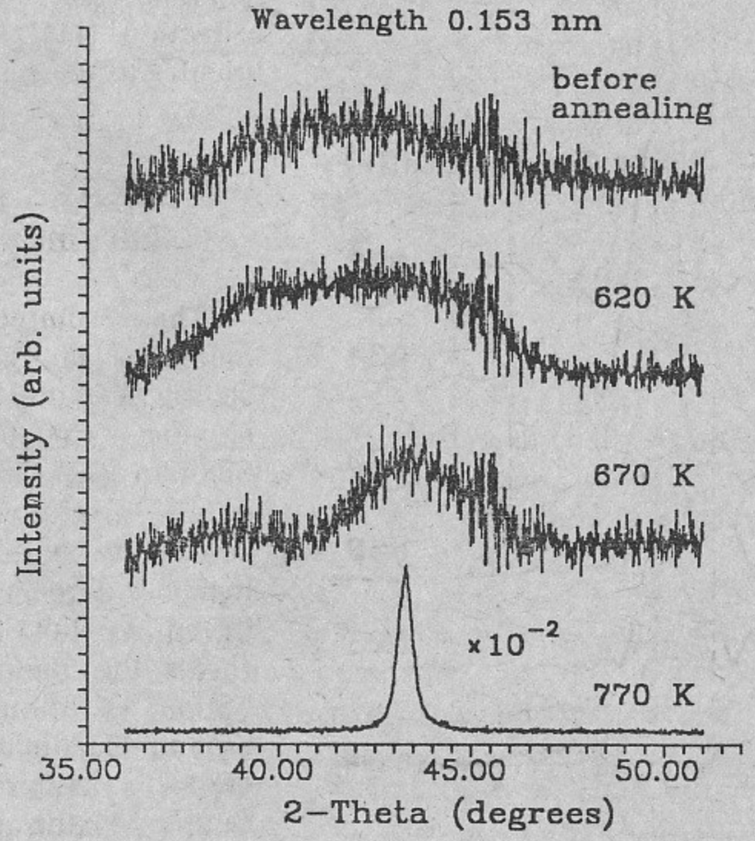

Fig.5 Diffraction patterns for Ni/C multilayer (sample 2) as a function of annealing temperature: a) without annealing; b) T=620 K; c) T=670 K; d) T=770 K (peak corresponds to the (111) reflex of crystalline nickel). The substrate background is subtracted.

670 K resulted in an appearance of the wide diffraction peak which corresponds to the (111) reflex of crystalline nickel. An ~3° angular width of reflex enabled us to evaluate the size of crystallites in the direction perpendicular to the mirror layers. This size was 27 Å. An-nealing at 770 K leads to a substantial increase of the reflex intensity (by a factor of 10^2). A 0.6° angular width of the (111) reflex corre-sponds to the crystallite size ~130 Å (about 3-4 periods of the mir-ror).

An analysis of the reflection intensities of the annealed samples (especially the absence of the (200) reflex) enabled us to conclude a dominant orientation of the direction of a dense packing (crystallographic direction (111)) perpen-dicular to the mirror lay-ers.

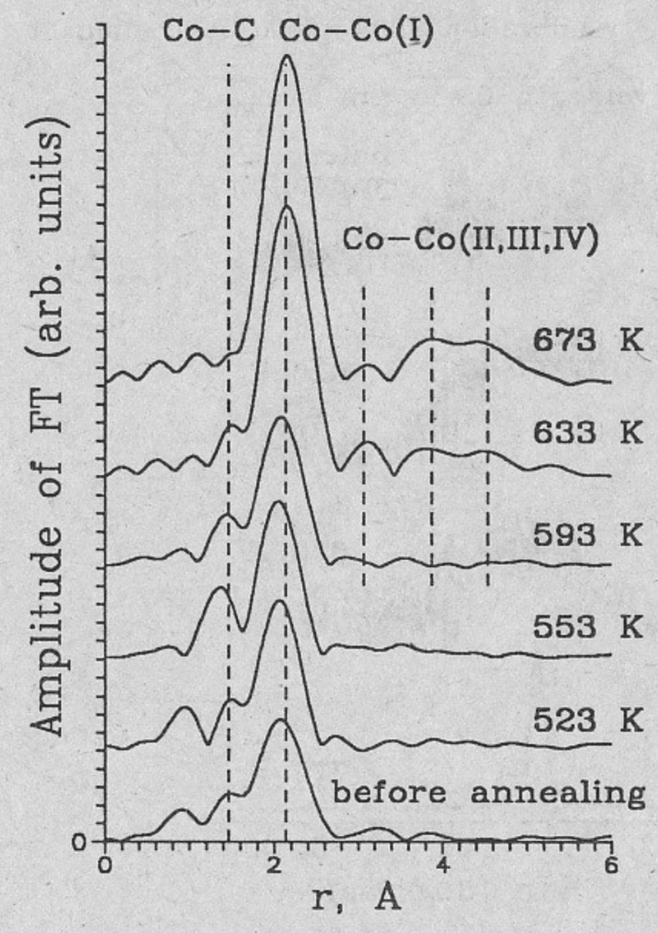

Fig.6 Cobalt K-edge Fourier transform of the K^3 - weighted fine structure (K- range=3-12 $Å^{-1}$) as a function of annealing temperature. Peak positions are uncorrected for phase shifts.

5. EXAFS mea-surements

The samples were measured on the EXAFS station of the VEPP-3 storage ring of the Siberian SR Center. For detailed information on conditions of measure-ments the reader is re-ferred to Ref [6]. Fig.6 shows the radial distri-bution of atoms (RDA) around Co depending on annealing temperature for sample 4 (the picture is given without taking into account the phase cor-rection). Coming from the character of changes of

RDA curves we can say the following.

1. Up to the temperature 590 K only two coordination spheres corresponding to distances Co-C, Co-Co are observed. Metal layers are in amorphous state.

2. With the annealing temperature range 590 to 630 K any signif-icant changes of the Co-C coordination sphere are not observed. The amplitude of the 1st Co-Co coordination sphere is increasing slowly. This fact may be explained by insignificant ordering of metal layers. However, the amorphous like nature is conserved.

3. At 630 K a decrease of the amplitude of the peak of the Co-C coordinate sphere, a strong increase of the amplitude of the Co-Co contribution and the appearance of the 2nd, 3rd, 4th coordination spheres of metallic Co are observed.

4. The further temperature growth leads to the disappearance of the Co-C peak. The RDA curve acquires the shape similar to that for polycristalline cobalt. This evidences the practically full separation of metal and carbon layers and an intense process of Co layers crys-tallization.

Note that similar EXAFS measurements on Ni/C multilayers did not give any significant changes to the picture of boundaries and layers formation.

6. Conclusion

The changes occurring in MLS during annealing can be grouped into three stages.

From 490 K to 600-620 K the intermediate layer disintegrates and this is accompanied with a simultaneous graphitization of carbon. The first order Bragg peak reflectance of MLS grows. There are no changes in the roughness of interfaces. At this stage of annealing no structural changes in the metal occur.

At 600-620 K the metal layer starts to crystallize. The shape of the EXAFS spectra sharply changes. The peak of the Me-Me bound increases approximately by a factor of two. The 2nd, 3rd and 4th metal coordination spheres are observed. The peak of the Me-C interaction reduces. The PXRD measurements show a narrowing of the diffraction peak (111) (crystallites increase in size). Here the sharpness of boundaries improves, although the roughness insignif-

icantly increases. At 670 K the peak of the Me−C bound disappears and the Me−Me bound grows. The roughness increases, but the structure of the multilayer still remains.

The third stage takes place at 770 K. The metal crystallites destroy the carbon layers and the MLS structure disappears.

It is interesting to note that for all Me/C structures where Me is a transition metal the catalytic mechanism of conversion of amorphous carbon to graphite takes place. In this case, the transition metal serves as a catalyst [8]. This mechanism brings about a sharp reduction of the graphitization temperature for carbon from 3000 K down to 600−700 K. This temperature coincidences with that at which the X−ray optical properties change during an annealing.

In our case the process of carbon graphitization accompanied with a simultaneous start of surface crystallization of the metal proceeds primarily in the intermediate layer. While disintegrating the inter−mediate layer, the epitaxial coordination of the graphite structures and metal (Ni and Co) in the (001) and (111) planes, respectively, takes place. There is the best agreement of the parameters of the (001) graphite planes and the (111) metal planes there is just for Ni and Co.

During annealing at even higher temperatures the metal layers convert into big globules sprouting through MLS. In this case the energy of the Me−Me interaction plays a more important role than the energy of the Me−C interaction.

Thus, the improvement of the X−ray optical characteristics of multilayers is achieved at the optimal annealing temperature corre−sponding to self−epitaxial catalytic delimination of the mixed layer. The exceeding of this temperature leads to the volumetric crystal−lization of the metal inside the layer and also to the rougher surface.

In conclusion, we wold like to note that the similar mechanism of self−epitaxial catalytic delimination of the interfaces of the Me layers is promising for the formation of structures of other types.

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EXAFS, PXRD and SAXS Studies of Annealing in Co/C and Ni/C Multilayers Manufactured by Pulsed Laser Evaporation Method

Э.П. Кругляков, С.В. Мытниченко, С.Г. Никитенко,
М.В. Федорченко, В.А. Чернов, Н.Н. Чхало

Исследование методами EXAFS, PXRD и SAXS влияния отжига на свойства Co/C и Ni/C многослойных рентгеновских зеркал

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