

CHEMICAL AND STRUCTURE TRANSITION IN METALLIC FILMS UNDER INFLUENCE OF ELECTRONS

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ABSTRACT

Results of investigation of structure and chemical transition in films Sc, Y and Cr at thermal annealing in vacuum chamber and when heating the films with an electron beam directly and microscope are performed.

Was received, what chemical composition of films at prolonged annealing was the same as and at annealing an electron beam.

We draw a conclusion that Sc_2O_3 is formed from metastable Sc, which is not observed in massive Sc.

INTRODUCTION

The investigation of structural and chemical transitions in condensed films at thermal annealing or under influence of charged particle beams (in particular, electrons) presents a considerable scientific and practical interest because electron ray treatment can be considered as radiation defects introduction process. Changing its rate can change kinetics and sequence of chemical transitions, which will produce various changes of film sample physical properties.

PROCEDURE AND EXPERIMENTAL TECHNIQUE

Films were condensed in a vacuum of 10^{-3} up to $5 \cdot 10^{-4}$ Pa produced by a diffusion oil pump. NaCl monocrystals or carbon films (for diffraction and microscopic investigations) were used as substrate at room temperature. Thickness of films and condensation rate were varied over a range as follows: $d \approx 30$ up to 200 nm and $w \gg 0,1$ up to 15 nm/s accordingly.

For diffraction and microscopic investigations were run using electron microscope (10^{-3} Pa). A plane spacing measurement accuracy was $\pm(0,001 \div 0,002)$ nm.

Films placed on a microscopic grate have been annealed in a vacuum chambers at $T=300,700$ K during 20 minutes with heating rate 7 K/min. Heating with an electron beam was 3 to 10 sec.

PHASE COMPOSITION OF CONDENSED AND ANNEALING FILMS

Scandium. The following phase composition is observed while condensation of films of all thickness studied proceeded:

- fcc - phase ScH_x with lattice parameters varying over a range of $a = 0,478$ up to $0,482$ nm, depending on thickness and conditions of formation; this phase transition to hcp - phase Sc during 1 to 2 months while aging;
- hcp - phase Sc with lattice parameters $a=0,325$ up to $0,334$ and $c=0,523$ up to $0,531$ nm, the phase undergoing no changes while aging;
- phase with distorted hexagonal lattice evolving during a few hours a fcc-phase or, alternatively, into fcc + hcp - phase composition.

Parameters of a lattice of the fcc- and hcp-phase are in a close agreement with a value of $a_0=0,478$ nm for a bulk ScH_2 (a lattice of a type of CaF) as well as with one of $a_0=0,3309$ and $c_0=0,5273$ nm for a bulk hcp - Sc [1]

Therefore the fcc-phase observed can be interpreted to be a ScH_x - hydride forming as result of interaction of hydrogen from a residual atmosphere. Electron-microscopic and diffraction examination of such films point to their having been of a fine- dispersion structure with negligible inclusions of some other phase giving 3 to 4 slight reflections on micro electron-diffraction patterns.

As it was afterwards turned out to be the these extra reflections correspond with intensive Sc_2O_3 - (112), (233), (134) lines. Sizes of oxide particles are no greater than 7 nm. Evidently, increase in a hcp - Sc lattice parameter is also associated with an influence of impurity atoms introducing into a lattice. Hydrogen seems to play here a major part of decrease in condensation rate or increase in pressure of gases leads to formation of ScH_x . Decrease in the lattice parameters as again a and c had been previously observed in thin films or in small particles of V, Cr, Zn, Gd, Bi, Au a.o. by different workers. This being usually accounted for by an effect of the Laplacian pressure, vacancy-origination and by other lattice defects.

It should be noted that decrease in a and c parameters had been observed by present writers in films obtained at a high condensation rate when an amount of gases dissolved gets negligible.

To summarize the foregoing let's note that a hydrogen content in the films under study may be qualitatively judged using the published information concerning the solid specimens. According to the X-ray diffraction studies [2] at a room temperature the hexagonal lattice is retained in the regions of Sc-H solution up to H/Sc concentration equal to 0.42, with which the ScH_x fcc- phase coexisting with hcp-Sc-H makes its appearance up to a concentration of 1.63. An interval of H/Sc=1.63 up to 2.00 corresponds to the monophase fcc- ScH_x region. It may be inferred from this evidence that hydrogen concentration in the hcp- ScH_x films is not more than 0.42, whilst in the fcc- ScH_x films - not less than 1.63.

These values may happen to be others by virtue of extension of solubility limits or homogeneity region usually observed in thin films.

The figure 1 is illustrated typical microstructure of films ScH_x at annealing in vacuum chamber and in microscope column.

Structural and phase transformations within a section of 30 mm arc observed in these films while annealing by means of electron beam in a microscope. Beyond this section an initial fcc - structure is retained. Recrystallization and formation of Sc_2O_3 crystals are resulted by the action of electrons.

Some peculiarities of these processes may be pointed to as follows. Crystal growth of a parent phase and Sc_2O_3 had been observed with approaching a center of the sector heating with an electron beam. A variety of moire patterns is observed within the region of intermediate heating of ScH_x , which is associated with an origination of Sc_2O_3 - crystals directly on the ScH_x - surface and with a close agreement between lattice parameters of hydride and oxide ($a_{\text{Sc}_2\text{O}_3} - 2a_{\text{ScH}_x} = 0,03 \text{ nm}$). The bands of moire patterns repeat contours of a surface of the phase articulation, which permits the oxide crystal sizes to be judged (average size being of $\sim 12 \text{ nm}$). Sc_2O_3 -crystals gain in size up to about 140 nm in the region of a maximum heating, and two-phase as it continues to remain no moire patterns are observed in the film, which seems to be associated with oxidation permeate entire thickness of a specimen.

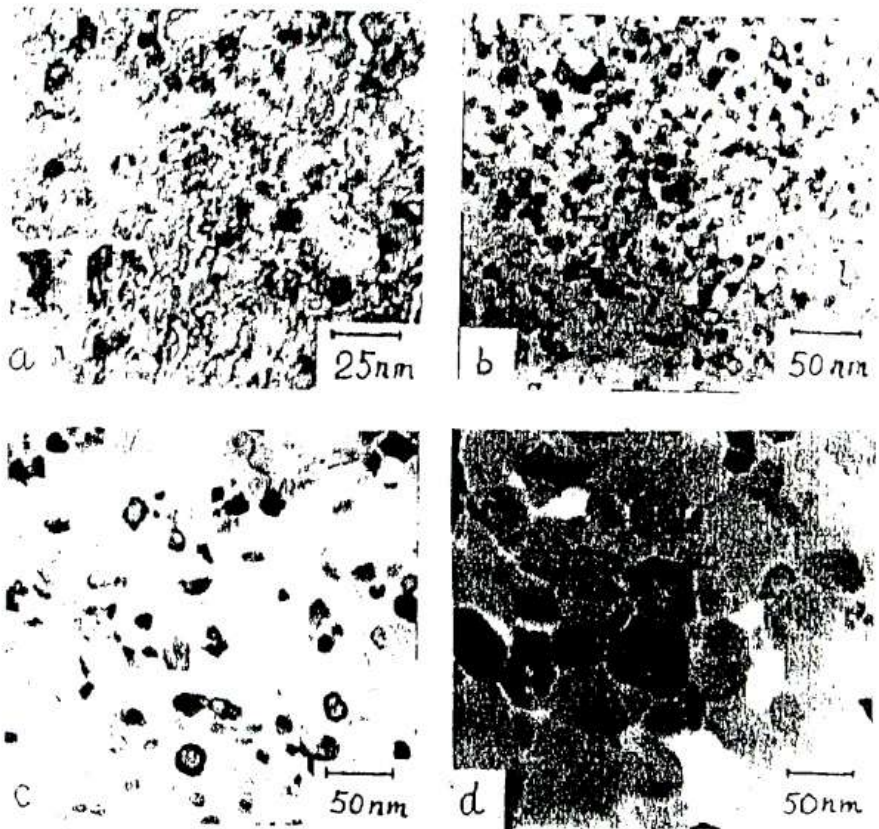


Fig. 1. Microstructure of $\text{ScH}_x + \text{Sc}_2\text{O}_3$ films obtain by annealing of ScH_x in vacuum chamber (a) and in electron microscope (b-d).

An intensive oxidation all over all over the film surface is also observed with the initial fine-dispersed hep. Sc-phase being heated with an electron beam, but without moire patterns specific to the previous case (due to difference between the Sc and Sc_2O_3 lattices). The Sc_2O_3 - crystals gain in size more than up to 2000 \AA in the region of maximal heating extinction contours being clear-cut.

To judge by diffraction images no marked alterations in the initial ScH_x -films containing Sc_2O_3 - and Sc-inclusions take place while annealing in a vacuum of $5 \cdot 10^{-7} \text{ Torr}$, up to 470 K , except for increasing in d_{hkl} . The most intensive Sc_2O_3 reflections become available over 470 K , their number being then continuously increased. Ranging from 570 K the fcc-lattice of ScH_x undergoes a tetragonal distortion

leading to splitting the (200)-, (220)-, and (311)-lines (at 870 K only the (311)-line remains splitted, while a (220)-reflection disappears). At this stage, both evolution of oxygen into a lattice appear to take place. Microstructure and diffraction image of the oxide obtained. Sc_2O_3 has bcc-lattice of the Mn_2O_3 -type with a parameter of $a=0,989$ nm, this being somewhat more than $a_0=0,981$ nm for bulk a specimens. Annealing in a superhigh vacuum gave the results as follow. ScH_x with Sc_2O_3 inclusions is not affected up to $T=420$ K ((200) fcc reflection disappears and (002) hcp appears at this temperature). $\text{fcc-ScH}_x \rightarrow \text{hcp-Sc} + \text{Sc}_2\text{O}_3$ transition takes place at temperature of 420 K, i.e. hydrogen diffuses from the lattice completely. A similar oxide formation (observed are altogether three Sc_2O_3 -reflections, these being (112), (233), and (004) ones) take place at $T=470$ K and when annealing an initial hcp structure as well (further annealing up to 670 K does not lead to any alterations). These results allow to draw a conclusion that oxygen available in a residual atmosphere, rather than that entering into a film in the course of condensation and subsequent withdrawal to atmosphere, is mainly responsible for oxidation.

Yttrium. YH_x fcc-phase or Y hcp-phase or $\text{YH}_x+\text{Y}+\text{Y}_2\text{O}_3$ is formed in Y films depending on condensation conditions. YH_x lattice parameter $a=0.529$ nm which is slightly larger than $a_0=0.520$ nm; in Y hcp-phase $a=0.374$ nm and $c=0.577$ nm, which are very close to $a_0=0.365$ nm and $c_0=0.578$ nm; Y_2O_3 bcc-phase (Mn_2O_3 type) has parameter $a=10.697$ nm, which is almost equal to $a_0=10.603$ nm. On thermal annealing of film samples in electron microscope column all regularities observed in Sc films are presented, which can be explained by Sc and Y physical and chemical properties proximity.

Chromium. Cr films phase composition corresponds to bcc-phase or to fcc-phase CrO_x ($a=0.414$ nm) on relatively small condensation rate, or to bcc-Cr+ Cr_3O . Cr_3O has b-W type lattice with parameter $a=0.458$ nm. Formation of oxide Cr_2O_3 with g- Fe_2O_3 type lattice and parameter $a=0.835$ nm (Fig. 2) takes place when films consisting of CrO_x , Cr+ Cr_3O and Cr annealed in vacuum chamber or in electron microscope column. Cr_2O_3 is stable up to temperature of 925 K. Transition Cr_2O_3 (hcp- $\text{Cr}_2\text{O}_3+\text{Cr}_3\text{O}_4+\text{CrO}_{2.6}$ takes place at higher temperatures.

Let's note that in all cases chemical transition temperature was estimated by graduation dependence using such characteristic points: ScH_x reduction temperature (fcc- ScH_x reflection (200) disappears and hcp-Sc reflection (002) appears on electron diffraction picture), which begins at T (420K and completely finishes at T (470K; phase transition temperature in Co films (T=690 K); temperature of reduction Co from CoO (T ((720÷750)K).

It should be noted that Cr_2O_3 oxide formation takes place when bombarding Cr film ($d=50$ nm) by Cr ions [3]. Cr_2O_3 (400) with $d_{hkl}=0.204$ nm line appears when ion dose is greater than 10^{11} m^{-2} .

Note that the Cr_2O_3 and Y_2O_3 oxides formation takes place in metals with bcc lattice. We draw a conclusion that Sc_2O_3 formation is also based on bcc lattice of Sc which is metastable.

As a result of conducted experiments the following conclusions can be made. Annealing of film materials in vacuum chamber or electron microscope column leads to the same chemical transitions but occur with different rates.

Stable Me_2O_3 oxide formation which takes place at any starting phase structure (Sc, Y, Cr; ScH_x , YH_x or CrO_x , Cr_3O) is common for all three studied metals.

Sc_2O_3 oxide formation, most probably, is based on metastable bcc-Sc modification.

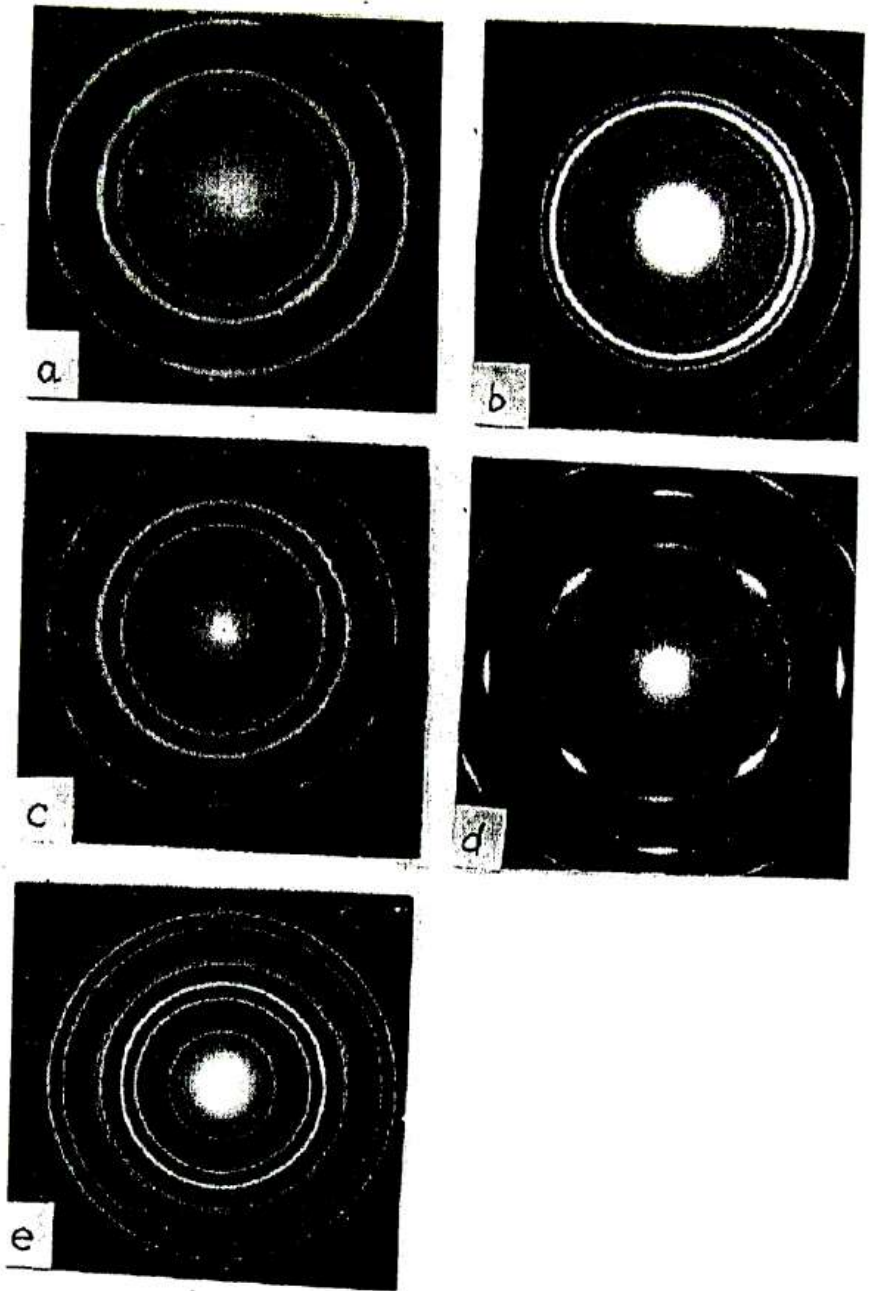


Fig.2. Electron diffraction patterns of CrO_x (a), Cr_3O (b), $\text{CrO}_x+\text{Cr}_2\text{O}_3$ (c), $\text{Cr}+\text{Cr}_2\text{O}_3$ (d) and Cr_2O_3 (e).

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