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Thin Solid Films 263 (1995) 42–46

thin solid films

Oblique growth of iron thin films on glass: a cross-sectional transmission electron microscopy study

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Received 17 October 1994; accepted 7 February 1995

Abstract

Very thin iron columnar layers have been obliquely grown on glass under ultra-high vacuum, and studied by cross-sectional transmission electron microscopy, selected-area electron diffraction and X-ray texture analysis experiments. Micrographs of layers a few tens of nanometres thick have been obtained. For the first time, we put forward the existence of an oblique growth for such thin layers in the case of metals. We discuss the influence of the inclination of the flux, and we compare our results with existing theoretical models. We also describe the influence of other parameters such as the substrate temperature or the divergence of the incident flux. We finally attempt to explain this columnar morphology by means of a Volmer–Weber growth and a shadowing effect.

Keywords: Growth mechanism; Iron; Surface morphology; Transmission electron microscopy

1. Introduction

Oblique columnar growth has often been theoretically studied, such as in ballistic deposition models [1] or continuous models [2]. This phenomenon is actually interpreted in terms of the shadowing effect created by atoms of the growing film. It only appears when the adatom mobility is limited but not zero.

Oblique layers generally exhibit anisotropic properties: magnetic [3], optical [4] or crystallographic [5] anisotropy. These properties strongly depend on the microstructure of the films. Direct observation of oblique columnar layers may provide important information: size and shape of the grains, the presence of grain boundaries or lower density zones, inclination of grains in relation to the normal of the surface.

Despite studies on amorphous layers such as SiO [6], transmission electron microscopy (TEM) has been little used in the case of very thin oblique metallic layers (a few tens of nanometres). For instance, Hashimoto and coworkers studied iron [7], cobalt [8] and aluminium [9] layers with thicknesses of about 1 μm on glass using replica techniques. Mbise et al. [10] used scanning electron microscopy to study layers some hundreds of nanometres thick of chromium, silver and aluminium.

The question is whether the strong columnar effect observed for thick metallic layers still appears in thin films. Indeed, optical transmission anisotropy is observed on thin layers [11], whereas observation of the microstructure is conducted on thicker layers. Conclusions on the influence of the morphology on optical properties are thus extrapolated. We propose here to examine the morphology of thin iron films which may be typically used for optical measurements.

In this article, the deposition of iron oblique columnar layers on float glass under ultrahigh vacuum (UHV) is described, and the advantages of this technique are emphasized. Then micrographs showing cross-sections a few tens of nanometres thick are presented. The crystallographic properties of these layers are also shown. Eventually, we demonstrate the influence of the deposition parameters on the microstructure, and compare our results with previous theoretical work.

2. Experimental details

2.1. Elaboration

Iron layers have been deposited on float glass in a molecular beam epitaxy (MBE) apparatus. The pressure during deposition was of about 10^{-8} Pa, which gives a mean free path of about 10^6 m. The incident flux can be considered as an atomic beam, without collision. The conditions of UHV also annihilate the presence of oxygen for example and therefore allow the production of very clean layers.

Iron is thermally sublimated from a Knudsen cell. The geometric specifications of the cell induce a very directive flux compared with a cosine law [12], which is appropriate for the study of oblique growth. The distance between the evaporation source and the substrate is 250 mm. We work with small rates of condensation from 0.2 to 1.5 nm min^{-1}.

Float glass substrates are cleaned with an alkaline solution in order to eliminate carbonate traces. They are in-situ outgassed at 400 K for a few hours. The cleanliness of the substrates and of the iron layers is checked in situ using Auger electron spectroscopy.

The geometrical specifications of the deposition apparatus allow a variation of the inclination of the incident flux from 0° to 80°. We chose different temperatures of deposition, from 300 K to 700 K. One of the advantages of the apparatus consists of disconnecting the parameters of deposition.

2.2. Cross-section preparation

The preparation of the cross-sections is derived from the method of Bravman and Sinclair [13] . In order to observe the iron layers in their inclination plane, we cut small tongues perpendicular to the direction of the incident flux.

The discs used for TEM observations are mechanically polished down to 150 μm. They are placed on a dimpler in order to slim the centre of the discs down to 50 μm. They are finally placed in an ion-beam thinning apparatus. The samples are rotated and chilled with liquid nitrogen during sputtering. Mechanical polishing is not taken too far because of the softness of the glass substrate. On the other hand, ion beam thinning is very fast despite the initial thickness of the samples.

The micrographs were shot with a Philips CM20 microscope and intrinsic analysis problems had to be faced. Indeed, the thinnest regions of the samples are not stable under the electron beam, especially in the case of very oblique films. Therefore a compromise had to be found between the right thickness for satisfactory micrographs and a thick enough sample to prevent instability. Moreover, the presence of iron induces the need for a regular adjustment of astigmatism.

2.3. Crystallographic-properties analysis

The crystallographic properties of these layers have been investigated through selected-area electron diffraction (SAED) and X-ray texture analysis. The experimental details concerning X-ray diffraction are explained in Ref. [14]. SAED is performed on cross-sections, using a selected diaphragm diameter equal to 1 μm. Such an experiment could not be carried out on the top of the surface. Indeed, the insulating behaviour of the substrate adds a diffuse background which makes the observation of the diffraction patterns difficult.

3. Results

3.1. Thin film morphology

The influence of incident-flux inclination (defined in Fig. 1) on the structure of layers prepared at 300 K was studied. In Fig. 2, the micrographs show cross-sections of iron layers prepared for α varying from 0° to 70°. The films prepared at $\alpha = 0°$ exhibit low diffraction contrasts which may explain the poor quality of the first micrograph.

A columnar structure was obtained for all values of α. In almost every case, grains grew throughout the thickness of the film. In other words the columns are monocrystalline. Layers are made of a dense structure with grain boundaries for $\alpha = 0°$, and consist of needles surrounded by zones of lower density when α increases.

We have measured the value of the inclination of grains β by calculating an average of a number of values. Fig. 3 provides the variation of β according to α. β reaches values from 50° to 60° in the most oblique films ($\alpha = 70$–$75°$).

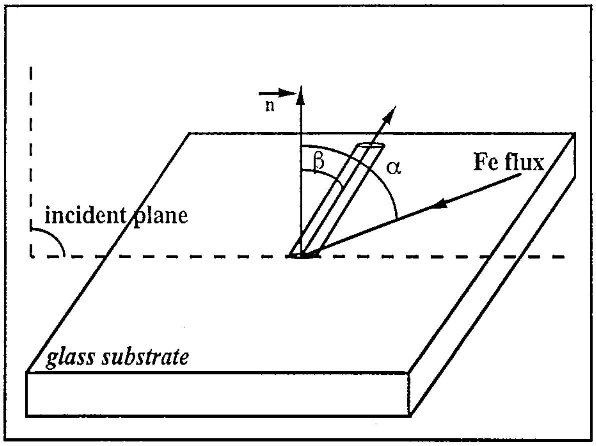

Fig. 1. Definitions of angle notation.

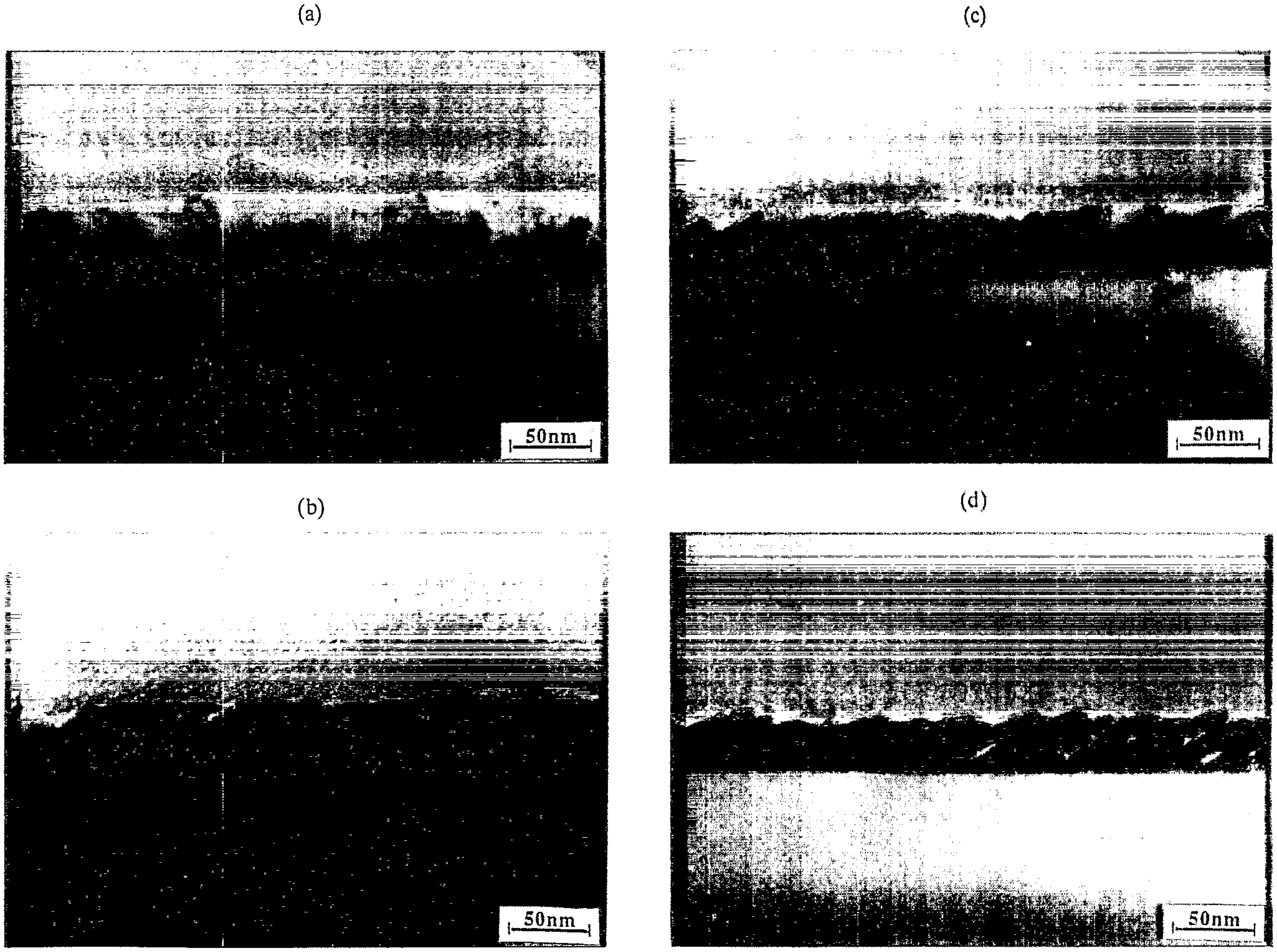

Fig. 2. Cross-sectional TEM micrographs showing iron columnar layers on glass, prepared at $T = 300$ K: (a) $\alpha = 0°$; (b) $\alpha = 50°$; (c) $\alpha = 60°$; (d) $\alpha = 70°$. Note the increase of inclination β and of contrast (the decrease of density) when α increases.

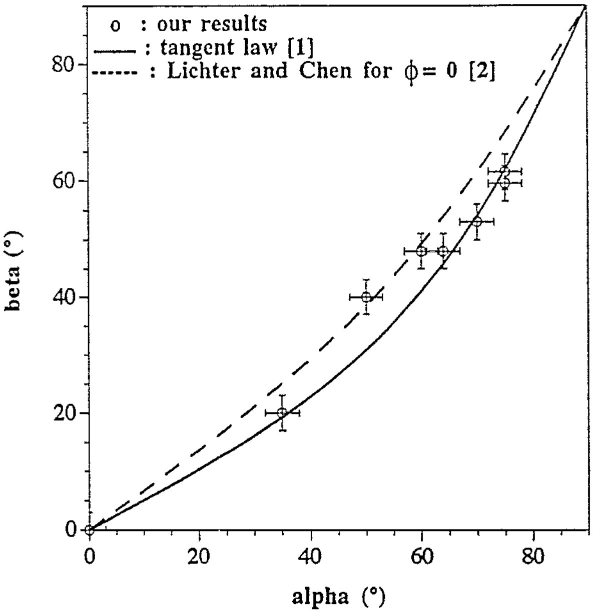

Fig. 3. Variation of the inclination angle β of columnar grains versus the incident angle α.

The last point in Fig. 2 deals with the distribution of the grains along the substrate. We observed that whatever the value of α is, the number of grains on a given distance remains constant. The value of α does not seem to have any influence on this distribution.

Iron on glass was also evaporated in the same apparatus through electronic bombardment of a spherical charge. In this case, the isoflux curves are wider and can be described by a cosine law. The films obtained through this technique possess the same characteristics as the previous ones but the inclination of the grains is less significant ($\beta = 50°$ when $\alpha = 80°$).

Finally, the micrograph in Fig. 4 shows the microstructure of a film prepared at $\alpha = 70°$ and $T = 500$ K. An increase in the temperature of the substrate destroys the oblique columnar structure and leads to the formation of wider grains, with a size of about 40 nm in the plane of the substrate.

3.2. Crystallographic properties

Texture analysis experiments [14] show that a layer elaborated at $T = 700$ K and $\alpha = 70°$ presents a $\langle 200 \rangle$

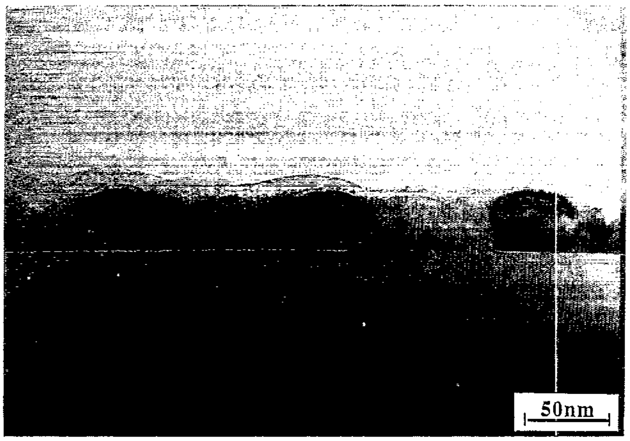

Fig. 4. Cross-sectional TEM micrograph showing an iron layer on glass prepared at $\alpha = 70°$ and $T = 500$ K. The oblique columnar structure is destroyed.

fibre-like texture inclined at 10° from the normal to the sample towards the direction of the evaporation source. At room temperature and when $\alpha = 0°$, thin films possess two texture components with ⟨110⟩ and ⟨200⟩ directions, both perpendicular to the sample plane. These textures are relatively dispersed around their mean position. At room temperature and when $\alpha = 70°$, the ⟨110⟩ pole figure shows four large zones of higher intensity situated at around 45° from the normal, and separated in the plane [15] . One of these positions points towards the incident flux. However, a great proportion of crystallites remains randomly oriented at room temperature whatever the inclination of the flux.

This result is confirmed by SAED performed on cross-sections. Indeed, diffraction patterns of layers elaborated at room temperature show diffraction rings characteristic of a polycrystalline film. To conclude, if a fibre-like texture is clearly observed for the samples prepared at high temperature, it is not the case for the samples prepared at room temperature. A few of the grains present a ⟨110⟩ orientation along the axis of the growth, but the majority of the grains are randomly oriented.

4. Discussion

Fig. 3 compares our experimental results on the inclination of grains with two theoretical models. The first is a semi-empiric law called the tangent law [1] and is derived from the shadowing effect:

$$\tan\beta = \frac{1}{2}\tan\alpha$$

The second is a continuous model proposed by Lichter and Chen [2]:

$$\tan\beta = \frac{2}{3}\frac{\tan\alpha}{1+\phi\tan\alpha\sin\alpha} \quad 0<\phi<3.7$$

Our experimental values are compatible with the tangent law. Therefore the shadowing effect accounts for our results.

The columnar structure of films prepared at room temperature and its destruction when the temperature increases, may be linked to a classification of microstructures described by Thornton [16]. If T_m is the melting point of iron, we find T/T_m equal, respectively, to 0.18 and 0.26 for T equal to 300 K and 500 K. The former belongs to Thornton's zone I, where the adatom mobility is limited and where columnar growth actually appears. The latter is near Thornton's zone II, where the physical processes are dominated by surface diffusion. The destruction of the columnar structure and the change of surface profile may be interpreted in terms of an increase in the iron-atom surface diffusion.

We use very low rates of condensation compared with other experimental studies [10]. Yet, columnar growth is a competition between growth rate and surface diffusion, which is low but not insignificant at room temperature. Moreover, iron is sublimated under UHV, whereas oxygen, for example, generally promotes columnar growth [10]. The conditions used in our study are a priori not suitable.

The fact that we obtain oblique columnar films under these conditions may be explained by other experimental parameters. The comparison between the sublimation from the Knudsen's cell and the evaporation from a spherical charge of iron underlines that the inclination of grains and the shadowing effect are more significant in the first case. Yet, the most important difference between these two techniques lies in the shape of the isoflux curves, which are wider in the second case. Rather than the angle of incidence of iron atoms, we can say that the divergence of the flux is an important parameter which influences the inclination of grains.

The last point of discussion deals with the distribution of grains and the crystallographic properties of the films. We have seen that, at room temperature, the density of grains along the substrate remains constant whatever the value of α is, and that the density of grains decreases with the substrate temperature. Moreover, almost all the columns are monocrystalline. Finally, there is no crystallographic correlation between the majority of the columns.

These results can be understood when assuming a Volmer–Weber growth of iron on glass. Then, the density of nucleation remains constant at room temperature and does not a priori depend on the inclination of the incident flux. The fact that the density of nucleation decreases with the temperature is also consistent with this assumption. Moreover, in this scenario, there is no reason for a crystallographic registry to develop between islands because of the amorphous behaviour of the substrate. Finally, monocrystalline islands should grow in such a process (no chemical impurities and no strain) leading to monocrystalline columns. The columnar growth observed here can then be explained by a Volmer–Weber growth of iron on glass and by the shadowing effect granted by the limited surface diffusion (compared with the incident flux). To our knowledge, this scenario has never been taken into account in thin-film growth simulations.

5. Conclusion

In this study, we have shown that we can visualize the microstructure of very thin (few tens of nanometres) oblique columnar films of metals, using cross-sectional transmission electron microscopy. We can then compare the morphology and the anisotropic optical properties of the same samples. The results concerning the columnar growth of thick films can be applied to thin films slowly grown under UHV. The shadowing effect well describes our results and the tangent law is checked. Nevertheless, the divergence of the incident flux affects the inclination of grains and should be taken into account. We have put forward the competition between the shadowing effect and the surface diffusion. Finally, the columnar structure obtained in the Fe/glass system can be explained by the combination of a Volmer–Weber growth of iron on glass and a shadowing effect.

Acknowledgement

This work was supported by Saint-Gobain industries.

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