

Crystal Structure of Evaporated MgO Films on Amorphous and Polycrystalline Substrates

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Thin films of MgO were prepared by deposition from the vapor phase on amorphous and polycrystalline substrates. Transmission and reflection electron diffraction were used to determine the orientation of the crystals in these MgO films. It was found that, on amorphous substrates initially at room temperature, the films possessed a crystal orientation which varied with film thickness. Films thinner than ≈ 500 Å showed a random orientation. As the film thickness was increased above ≈ 500 Å, a [111] preferred orientation was developed with an axis inclined away from the substrate normal and toward the direction of the vapor beam at oblique vapor incidence. At high substrate temperature (≈ 150 – 300°C), the films followed the same behavior during growth. This preferred orientation is interpreted as a final growth orientation. On silver films as substrates, initially at room temperature, the same [111] preferred orientation was observed in films $\lesssim 100$ Å thick and with increasing film thickness the orientation persisted. In thick deposits a slight inclination of the orientation axis was also observed at oblique vapor incidence. These results suggest that on Ag substrates the orientation is an initial nucleation orientation and also a final growth orientation.

INTRODUCTION

Many electron-diffraction investigations have shown that crystals of films formed by deposition from the vapor phase on amorphous substrates tend to grow in a preferred orientation ("fiber texture").¹ The preferred orientation may be a one or two degree orientation, depending on whether only one or two crystallographic axes of most crystals point in preferred directions.

The preferred orientations in evaporated films with NaCl structure (e.g., various alkali halides) on amorphous substrates have been the subject of many experimental investigations.^{2–8} LiF^{2–7} and NaCl^{2,8} films evaporated at room temperature at normal incidence were found to possess a crystal structure which varied with film thickness. Films thinner than ~ 100 Å showed some degree of one-degree [100] orientation and as the film thickness was increased there was a change, first, to a completely random structure and then to a one-degree preferred orientation which was [111] for LiF and [110] for NaCl. The same [111] orientation was, however, observed in LiF^{2,7} and NaCl² films when these films were deposited indirectly, i.e., on the backside of the substrate, indicating that this orientation is characteristic for mostly random evaporation due to reflection, scattering, and reevaporation of molecules. It has also been observed² that, with increasing film thickness, there was a tipping of the orientation axis when the deposition was not normal to the substrate. For NaCl, the orientation axis tipped toward the direction of incidence of the vapor beam, and for LiF, away from it. Schulz² suggested that the tipping of the orientation axis away from or toward the direction of the vapor beam might be due to limited atomic mobility on the surface of the deposit.

Evans and Wilman⁸ suggested that the small inclination of the [111] orientation axis away from the vapor-beam direction, observed in LiF films,² may originate from the preferential growth of those crystals having main faces (planes of dense atomic packing) nearly normal to the oblique vapor beam. These authors

also suggested that the oblique orientations developed at oblique vapor incidence in thick deposits with low atomic mobility may originate from the surface roughness of the deposit and the attainment of sufficient mobility to favor the growth of those crystals with free surfaces in the form of certain faces.

Recently, Bauer¹ critically reviewed the interpretations of preferred orientations in evaporated films with NaCl structure. He distinguished between initial orientations and final growth orientations. Initial orientations can be due to nucleation or growth, depending on whether the interaction between the deposit and substrate is weak or strong. The driving force to form these initial orientations is the tendency of the deposit crystals to develop a minimum free energy configuration. The [100] orientation observed in thin films of LiF^{2,5,6} and NaCl^{2,8} deposited on amorphous substrates at room temperature is one of the best-established nucleation orientations.

Bauer suggested that the final growth orientations, which appear only in thick films—here all crystals have the same (not necessarily minimum) free energy configuration—are due to differences in the number of vapor molecules condensing on differently oriented crystals. An example, is the [111] orientation formed in thick films of LiF^{2,–4,7} evaporated at room temperature at normal incidence onto amorphous substrates. The orientations adopted in evaporated films may, then, be influenced by factors such as the angle of incidence of the vapor beam with respect to the substrate and the relative growth rates for planes of dense atomic packing. The observations¹ that these factors are also influenced by the presence and absorption of residual gases may explain the limited success thus achieved in formulating a single theory to account for the various observed preferred orientations. Thus, more experiments under defined conditions are still necessary to reach a quantitative understanding of the orientation phenomena in thin films. The aim of this paper, therefore, is to describe observations made on preferred orientations in MgO films prepared by evapora-

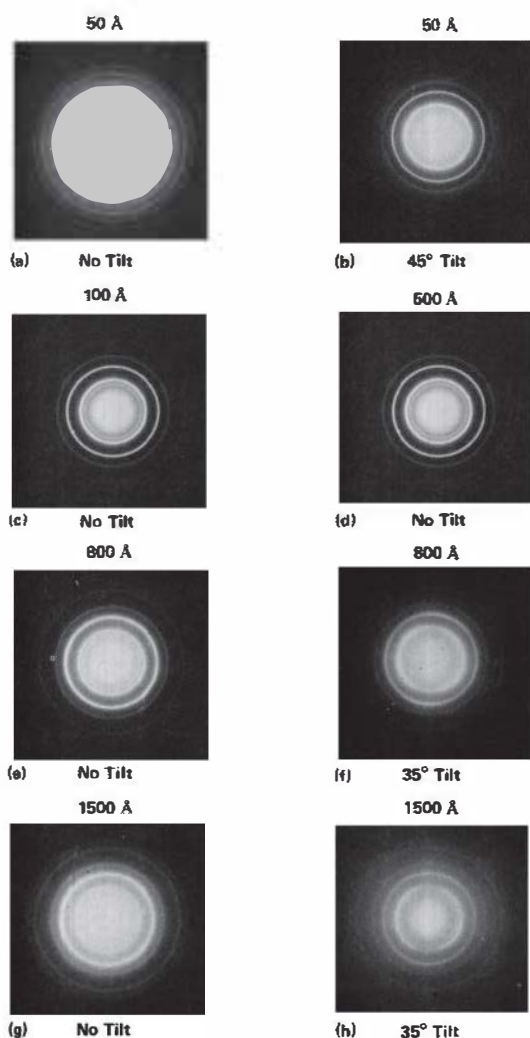


FIGURE 1. Transmission patterns of MgO films showing the change in the relative intensity of the diffraction rings as the film thickness is increased. The thicknesses are (a) and (b) ~ 50 Å; (c) 100 Å; (d) 500 Å; (e) and (f) 800 Å; (g) and (h) 1500 Å. In (a), the film is normal to the electron beam and in (b) the same film is tilted 45° . In (c) and (d), the films are normal to the beam. In (e) and (g), the films are normal to the beam, and in (f) and (h) the same films are tilted 35° .

tion onto amorphous and crystalline substrates. MgO resembles, for example, LiF and NaCl in that they all have a NaCl structure. The effects of film thickness, angle of incidence of the vapor beam, and substrate temperature on the orientations have been studied in the present investigation.

EXPERIMENTAL PROCEDURE

MgO films were deposited with a 6-kw electron gun. 99.95% pure MgO was used as "starting" material. A pressure of 2×10^{-6} Torr was obtained in the evaporator before evaporation, but this increased to 1.5×10^{-5} Torr during evaporation. The evaporations were performed without introducing oxygen. A shutter was placed close to the vapor source to shield the substrate from the source during the beginning and the end of an evaporation. The films were deposited at a rate of 3–5 Å/sec. The average thickness of the deposit and rate of deposition were determined by a quartz crystal located close to the substrate. Calibration was

performed by mounting a glass slide on the specimen holder and measuring the film thickness by a Zeiss interference microscope. The thickness range investigated was from about 50 to 7000 Å.

Glass cover slips were used as substrates. The substrates, after chemical and ultrasonic cleaning, were out-gassed at 300°C for about 1 h in the vacuum. A dc glow discharge, using 10-kV and 150-mA at 0.02 Torr argon pressure, was also used to clean the substrate surface immediately before the evaporation was performed. The initial substrate temperature varied from room temperature to 300°C . The substrates were held at different angles to the vapor beam so that the effect of the angle of incidence of the vapor beam with respect to the substrate could be investigated. To study the effect of the nature of the substrate, a 5000-Å thick film of Ag was evaporated from a tantalum boat on the glass substrates prior to MgO film evaporation.

Structural studies were carried out by means of electron diffraction and microscopy using a Phillips EM-100C electron microscope which could be adapted for reflection diffraction. The microscope was operated at 40–80 kV. Carbon-coated electron microscope grids were used as substrates for transmission electron diffraction and microscopy studies. To prevent charging up of the specimens in the electron beam during reflection electron diffraction studies, the edges of the specimens were painted with "Aquadag." The value of the glancing angle α was about 1° .

EXPERIMENTAL RESULTS

The angles β and δ denote the inclination of the vapor beam and the orientation axis, respectively, from the

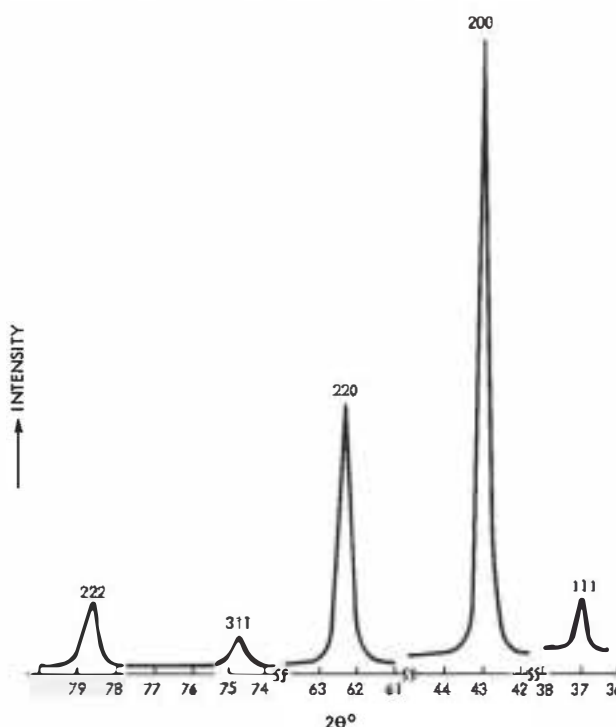


FIGURE 2. X-ray diffractometer trace for a randomly oriented MgO specimen.

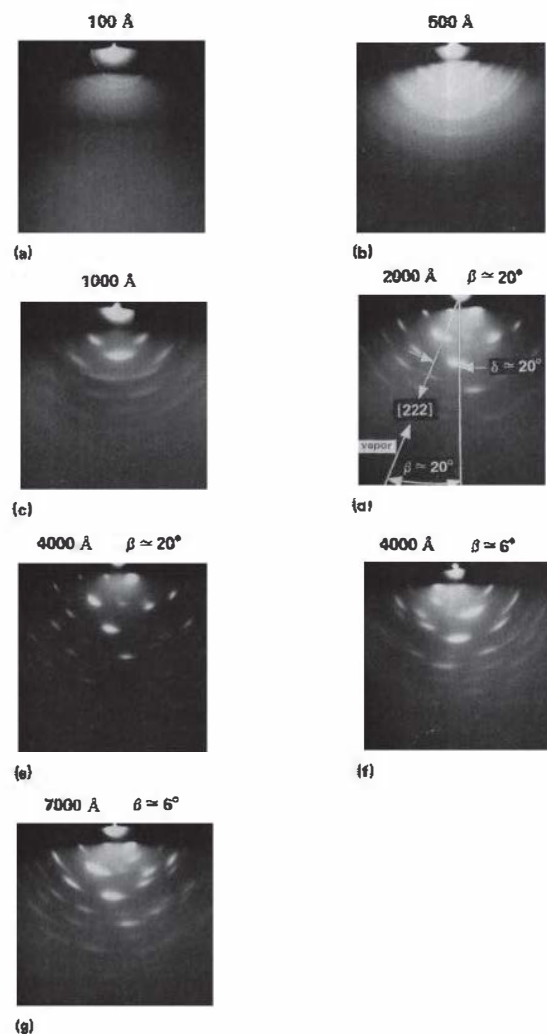


FIGURE 3. Reflection patterns from MgO films evaporated onto a glass substrate at room temperature. The patterns show the change in surface orientation as film thickness increases. The thicknesses are (a) 100 Å; (b) 500 Å; (c) 1000 Å; (d) 2000 Å; (e) 4000 Å; (f) 4000 Å; (g) 7000 Å. Patterns shown in (d), (e), (f), and (g) were taken with the electron beam in the B azimuth (see text).

substrate normal. The A and B azimuths of the electron beam, respectively, denote the directions parallel and perpendicular to the plane of incidence of the vapor beam.

Films of various thicknesses deposited on carbon substrate initially at room temperature were examined by transmission. Typical results given in Fig. 1 show a definite change in the relative intensity of the diffraction rings as the film thickness increases. Comparison of the relative line intensities for the transmission pattern (a) with those for the randomly oriented MgO structure (Fig. 2) shows a random orientation. Pattern (c) still shows a completely random orientation. The films producing patterns (a) and (c) gave no arcing of the diffraction rings when inclined to the electron beam as shown in pattern (b). As the film thickness increases, patterns (d), (e), (f), (g) and (h) show the development of a $[111]$ preferred orientation. The most significant changes are (1) the diminution of the (200) and (400) diffraction rings and (2) the increase in the rela-

tive intensity of the (220) diffraction ring. Furthermore, arcing of the rings was observed when the films were inclined to the electron beam. This is shown in patterns (e), (f), (g) and (h). In patterns (e) and (g) are shown, respectively, a 800- and a 1500-Å-thick film normal to the beam, and in (f) and (h) the same films tilted at an angle of 35° to the electron beam.

Figure 3 shows the general characteristics of the reflection electron diffraction patterns given by MgO films deposited on glass substrates initially at room temperature. The angle of incidence of the vapor beam, β , varied from $\sim 6^\circ$ to 20° . Electron diffraction by reflection failed to give distinct patterns for films thinner than about 100 Å.

At 100 Å a random orientation was observed. The diffraction patterns of Fig. 3 show that as the film thickness increases a 1° orientation develops. Detailed analysis of these patterns showed that the orientation was $[111]$. The patterns also indicate that the orientation becomes more pronounced as the film thickness increases.

In thick deposits, the orientation axis (with about $\pm 15^\circ$ angular spread or less from the mean as shown by the arc lengths in the diffraction patterns) was inclined away from the substrate normal and toward the direction of incidence of the vapor beam at oblique vapor incidence. This is shown in patterns (d), (e), (f), and (g) of Fig. 3, which were obtained with the electron beam in the B azimuth. The angle between the orientation axis and the substrate normal, δ , was approximately equal to β in the range of β between $\sim 6^\circ$ and 20° . The transmission and the reflection data, thus, show that MgO films on amorphous substrates possess a random structure in the range of thickness from ~ 50 to ~ 500 Å. There is, however, a definite change from a random structure to a $[111]$ preferred orientation as the film thickness increases above ~ 500 Å. This growth behavior is similar to that reported for LiF²⁻⁷ films evaporated at room temperature onto amorphous substrates. They differ only in that no $[100]$ preferred orientation was observed in thin films of MgO.

Films deposited on glass substrates initially at 150 – 300°C followed the same behavior during growth. Typical results, obtained for films deposited at 200°C at an angle β of 20° , are shown in Fig. 4. The patterns of Fig. 4 show that the same $[111]$ preferred orientation develops as the film thickness increases above ~ 500 Å. The results also show that the orientation axis is still

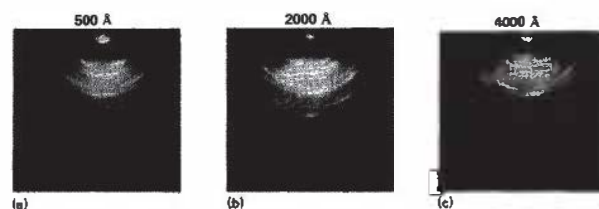


FIGURE 4. Reflection patterns from MgO films evaporated onto a glass substrate at 200°C . The thicknesses are (a) 500 Å; (b) 2000 Å; (c) 4000 Å. Patterns (b) and (c) were taken with the electron beam in the B azimuth (see text). The angle of incidence of the vapor beam β is 20° .

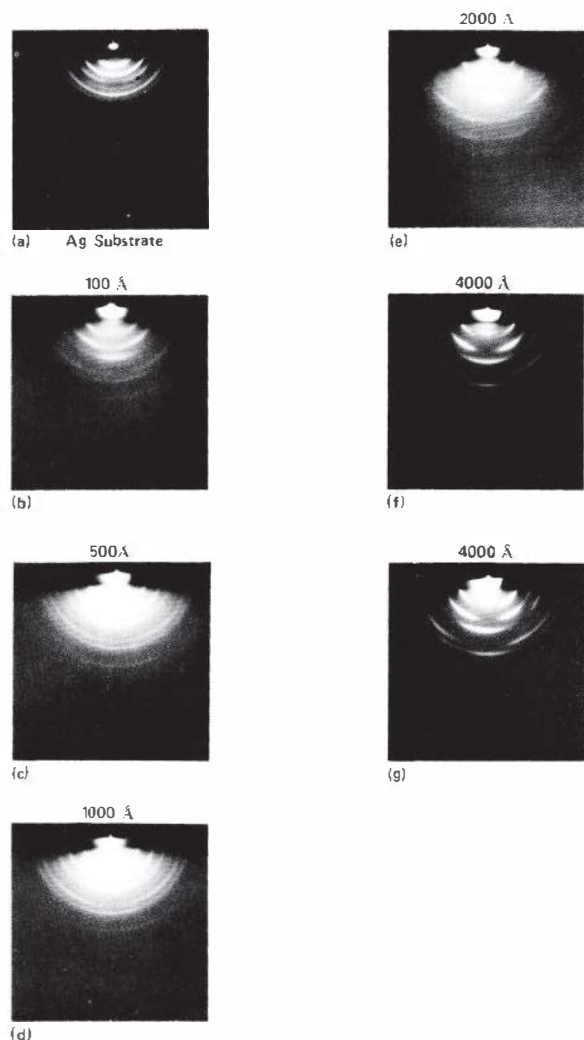


FIGURE 5. Reflection patterns from MgO films evaporated onto crystalline Ag films (a) at room temperature. The thicknesses are (b) ≤ 100 Å; (c) 500 Å; (d) 1000 Å; (e) 2000 Å; (f) and (g) 4000 Å. Pattern (f) was taken with the beam in the A azimuth and (g) with the beam in the B azimuth (see text).

tipped toward the direction of incidence of the vapor beam at oblique vapor incidence.

The reflection patterns produced by MgO films evaporated onto glass substrates, which were first covered with a 5000 Å thick film of evaporated Ag, at room temperature are shown in Fig. 5. The patterns obtained for the Ag films showed a random structure with some degree of [100] orientation [Fig. 5(a)]. The results in Fig. 5 show that (1) the same [111] preferred orientation is developed and (2) the degree of orientation increases with increasing film thickness.

The results also indicate that the orientation axis is slightly tipped toward the vapor beam direction at oblique vapor incidence. This is illustrated in patterns (f) and (g) of Fig. 5. Pattern (f) was taken with the electron beam in the A azimuth and pattern (g) with the beam in the B azimuth. It is interesting to note that on rough Ag substrates, ≤ 100 -Å-thick films have some degree of [111] preferred orientation [Fig. 5(b)], while on smooth glass substrates they have a random orientation. This illustrates the importance

of the nature and roughness of the substrate surface on the initial orientation.

Bright and dark field microscopy was carried out to observe the MgO films which showed some degree of [111] orientation. The dark field image was taken with a portion of the 220 diffraction ring. A bright and dark field view of an 800-Å-thick film is shown in Figs. 6(a) and 6(b). The transmission pattern in Fig. 6 indicates some degree of [111] orientation. The bright areas in the dark field view are images of crystallites oriented such that they diffract electrons into the particular portion of the 220 ring used for imaging. The film appeared to be continuous and the average crystallite size was observed to be about 300 Å. The crystallite size was measured, directly from the dark field image, perpendicular to the direction of the spherical aberration streaks.

DISCUSSION

The present results show that ~ 50 -500-Å-thick films of MgO (which has a cube equilibrium form¹) evaporated onto amorphous substrates at a temperature in the range from room temperature to 300°C have a random orientation. This initial orientation is different from that reported for many thin films with NaCl structure (e.g., various alkali halides). A [100] orientation was observed in LiF,^{2,5,6} NaCl,^{2,8} and NaF^{6,9} films evaporated onto amorphous substrates at room temperature. At high substrate temperatures (~ 300 -400°C) a weak [100] orientation was observed, while at intermediate temperatures (~ 150 -300°C) no orientation was found.⁶

The initial random orientation observed in MgO on amorphous substrates is thought to be formed as

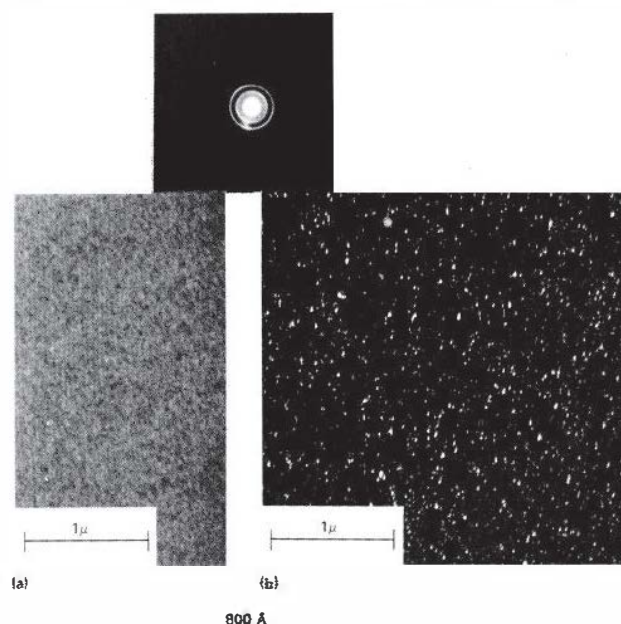


FIGURE 6. (a) Bright-field electron micrograph of 800-Å-thick MgO film. (b) Dark-field electron micrograph of the same film. The bright regions are images of crystals oriented such that they diffract the incident electron beam into a portion of the 220 diffraction ring. Note the aberration streaks which point upward in the micrograph.

follows. Residual gas molecules (strongly adsorbed on the substrate surface, thus reducing the interaction between the deposit nuclei and substrate) are expected to be removed by heat treatment and ion bombardment prior to film deposition. At a pressure of 10^{-5} Torr during film deposition, the substrate surface will, however, be covered with residual gas molecules at room temperature. The vapor molecules can then lose some of their excess energy by transferring it to the adsorbed gas molecules. The lifetime of the residual gas molecules on the substrate surface is reduced, while that of the vapor molecules is increased. Thus, the interfacial interaction between the deposit ions or molecules and substrate atoms can be assumed to be quite strong.

As a result of the high binding energy of the deposit ions to the substrate surface in this case, the surface mobility is decreased, the nucleation rates are high, and, owing to the more or less random arrangement of the substrate atoms, no preferred orientation is induced. The deposit ions or molecules tend to be densely packed but have random orientation. On the other hand, if the interfacial interaction between the deposit ions and the substrate atoms is weak, the nucleation rates are lower, and a [100] orientation may then be expected to be preferred since this orientation best minimizes the interfacial and surface free energies. This is not what has been observed experimentally.

With increasing film thickness, a [111] orientation develops with an axis tipped toward the direction of the vapor beam at oblique vapor incidence even at high substrate temperature. This suggests that the orientation is influenced by the vapor supply which favors the [111] orientation. The [111] orientation can then be interpreted as a final growth orientation originating not from a tendency to develop a minimum energy configuration but, rather, from the growth competition between differently oriented crystals due to differences in the number of vapor ions or molecules condensing on these crystals, (i.e. the orientation is due to the angular dependence of the condensation coefficient) as suggested by Bauer.^{1,10}

The present results also show that, on Ag substrates at room temperature, the same [111] preferred orientation appears in films as thin as $\lesssim 100$ Å and persists with increasing film thickness. This suggests that the orientation originates during nucleation. The slight inclination of the [111] direction toward the vapor beam at oblique vapor incidence in thick deposits indicates

that the orientation is also influenced by the supply of vapor ions or molecules which favor the [111] orientation. The [111] preferred orientation is thus interpreted as an initial nucleation orientation and also a final growth orientation. A detailed explanation of the origin of the initial orientation must, however, await the results of further experiments in progress in which MgO films are being deposited on [100] and [111] oriented Ag substrates.

CONCLUSION

Thin films of MgO prepared by deposition from the vapor phase on amorphous substrates initially at room temperature possess a crystal orientation which varies with film thickness. Films thinner than ~ 500 Å show a random orientation. As the film thickness increases above ~ 500 Å, a [111] preferred orientation develops with an axis tipped toward the direction of the vapor beam at oblique vapor incidence.

At high substrate temperatures (~ 150 – 300°C), the films follow the same behavior during growth. This preferred orientation is interpreted as a final growth orientation.

On silver films as substrates, initially at room temperature, the same [111] preferred orientation is observed in films $\lesssim 100$ Å thick and with increasing film thickness the orientation persists. In thick deposits a slight inclination of the orientation axis is also observed at oblique vapor incidence. These results suggest that on Ag substrates the orientation is an initial nucleation orientation and also a final growth orientation.

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