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METALLURGICAL AND PROTECTIVE COATINGS

INTERNAL STRESS AND STRUCTURE OF EVAPORATED CHROMIUM AND MgF_2 FILMS AND THEIR DEPENDENCE ON SUBSTRATE TEMPERATURE

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The internal stress in chromium and MgF_2 films was measured by the cantilever beam method. The substrate temperature, which was kept constant during the film deposition, could be varied up to 500 °C. At room temperature both materials exhibit only tensile stress over the whole thickness range. At higher temperature for both materials compressive as well as tensile stresses are found as the film thickness increases. Similar stress *versus* thickness curves have previously been obtained for the low melting point metals silver, copper and gold deposited at room temperature. The model for the origin of the internal stress proposed to interpret the stress curves of the metals of the copper group is again applicable. Thus the changes in the stress curves obtained at different substrate temperatures can again be correlated with changes in the growth mode and thus the structure of the respective films. The structure determined on the basis of the stress model agrees with the film structure visible in the electron microscope.

1. INTRODUCTION

We have used internal stress measurements in the past to study the growth of thin metal films and its dependence on a number of deposition parameters. The cantilever beam principle was used to measure the film stress. As discussed earlier[1], the temperature of the bending beam has to be kept constant to eliminate bending of the beam due to the bimetallic effect. In all previous experiments we controlled the substrate temperature, *i.e.* the temperature of the bending beam, by regulating the temperature of the housing surrounding the stress-measuring apparatus with water from a thermostat, and variations in the substrate temperature were thus limited. It is well known that the substrate temperature, among all the deposition parameters, most strongly affects the growth and structure of evaporated films by influencing the surface and volume diffusion of the deposited material. In order to investigate the influence of this deposition parameter as well we designed a stress-measuring device which allows the continuous determination of the film stress during the film deposition at any substrate temperature up to about 500 °C. In the present paper we report on first experiments with this experimental set-up in which we studied the internal film stress of chromium and MgF_2 films at different substrate temperatures.

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Both materials have been investigated in detail at room temperature by various investigators[2–8] and in our laboratory[9,10]. At room temperature these materials exhibit only tensile stress over the whole thickness range. In terms of a model for the origin of the internal film stress which we have published previously[11,12], the magnitude of this tensile stress indicates a dominant influence of the grain boundary relaxation mechanism and thus a small average grain size. The small changes in incremental stress furthermore suggest that this grain size remains more or less constant as the film thickness increases and therefore columnar grain growth is representative of the growth of the film. The stress curves of these materials differ considerably from those of the more mobile low melting point metals (silver, copper and gold) where changes in the incremental stress and even compressive stresses were found at certain growth stages. Since these compressive stresses cannot be explained as due to thermal effects (*i.e.* a temperature gradient through the glass beam or a bimetallic effect due to heat transfer from the evaporation source[1,13]) it has to be assumed that they are characteristic for the growth of the metals of the copper group and in terms of our model indicate varying grain size as the film thickness increases. With this in mind we have started the investigation presented in this paper, expecting that both chromium and MgF_2 deposited at higher substrate temperatures should exhibit compressive as well as tensile stresses because of an increasing mobility at higher temperature.

2. EXPERIMENTAL DETAILS

The intrinsic stress of the deposited films was measured with a bending beam apparatus described earlier[11,14]. With a glass beam of thickness 0.22 mm the sensitivity of the apparatus was approximately 10 dyn cm^{-1}. Positive values are assigned to tensile and negative values to compressive stresses. The temperature of the bending beam apparatus as a whole was controlled by the energy radiated from a heater (Ni–Cr wires (0.2 mm in diameter) in Al_2O_3 tubes (1 mm in diameter)) mounted inside the stainless steel housing (see ref. 14, Fig. 1). In all previous experiments this housing was held at room temperature with a water thermostat. An Ni–(Ni–Cr) thermocouple was positioned next to the bending beam as a sensor for the programmable temperature control[15]. For equilibration before each experiment the temperature of the bending beam was kept at the predetermined value for about 2 h. The temperature was regulated to better than 0.5%. The temperature changes due to opening and closing of the shutter at the start and the end of the deposition were less than 1% and were compensated for within a few seconds.

The base pressure of $(1\text{–}2) \times 10^{-7}$ Torr was obtained by using an oil diffusion pump with additional liquid-nitrogen-cooled traps. For the MgF_2 experiments the material was deposited directly onto the glass beam. Before the chromium evaporation an MgF_2 layer (mean thickness, about 150 Å) was deposited immediately before the metal to reduce or eliminate the effect of contamination layers on the surface of the bending glass beam. Both the chromium and the MgF_2 were evaporated from resistance-heated tantalum crucibles at an evaporation rate of 2 ± 0.1 Å s^{-1}. The mean thickness of the films was measured with a quartz crystal oscillator which was kept at room temperature outside the steel housing. The distance between the evaporators and the specimen was fixed at 20 cm.

3. RESULTS

3.1. Influence of the substrate temperature on the internal stress of MgF_2 films

As can be seen from Fig. 1, curve a, MgF_2 films deposited at room temperature exhibit only tensile stress over the whole thickness range investigated ($d < 8000$ Å) with a constant incremental film stress of 5.7×10^9 dyn cm^{-2}. This value is reduced to 2.9×10^9 dyn cm^{-2} when the film is deposited at a substrate temperature of 200 °C (Fig. 1, curve b). At 300 °C (Fig. 1, curve c) for the first time a tensile stress maximum develops at a mean thickness of about 70 Å. As the film thickness increases further, the internal stress of the MgF_2 film becomes compressive with a maximum force per unit width of -3200 dyn cm^{-1} at a mean thickness of 510 Å. Beyond this thickness the internal stress of the MgF_2 film is finally tensile with an incremental stress of 1.56×10^9 dyn cm^{-2}. Increasing the substrate temperature to 340 °C (Fig. 1, curve d) has little effect on the tensile stress maximum at about 70 Å but considerably increases the thickness range in which the film stress is compressive. The compressive stress maximum is shifted to a mean thickness of 2100 Å and to a force per unit width of 2.02×10^4 dyn cm^{-1}. The final incremental film stress is again tensile at 1.1×10^9 dyn cm^{-2}. When an MgF_2 film is evaporated

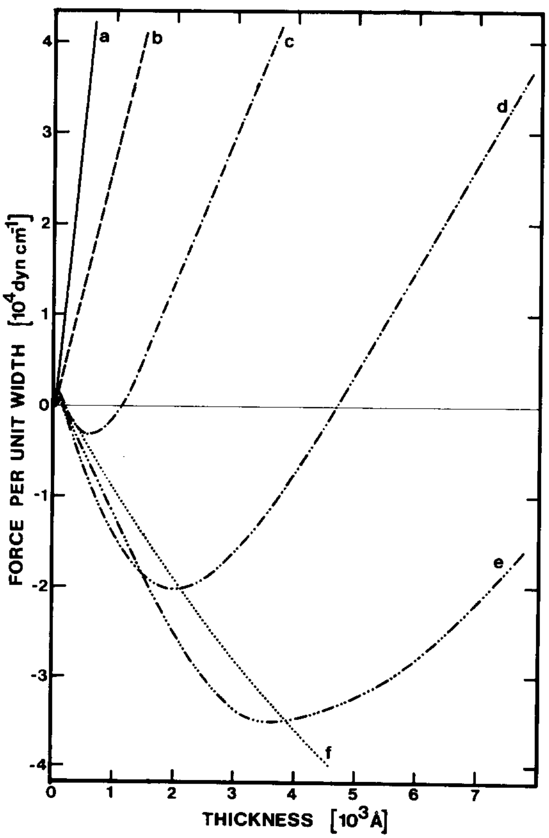

Fig. 1. Dependence of the internal stress of MgF_2 films on the substrate temperature: curve a, 25 °C; curve b, 200 °C; curve c, 300 °C; curve d, 340 °C; curve e, 360 °C; curve f, 460 °C.

at a substrate temperature of 360 °C (Fig. 1, curve e), the film stress is compressive up to a mean thickness of 3800 Å with a force per unit width of $-34\,400$ dyn cm^{-1}. The final incremental stress above this thickness is again lower at 7.4×10^8 dyn cm^{-2}. When the substrate temperature is increased to 460 °C the film stress (Fig. 1, curve f) is compressive over the whole thickness range with the exception of the small tensile stress up to a thickness of about 80 Å.

3.2. Influence of the substrate temperature on the internal stress curve of chromium films deposited onto MgF_2 substrates

As in our previous experiments with the metals of the copper group an MgF_2 film was deposited onto the glass beam before the evaporation of the chromium film to ensure reproducible substrate conditions. At room temperature the chromium stress *versus* thickness curve (Fig. 2, curve a) shows small changes in the incremental film stress up to a mean thickness of about 200 Å with a maximum value of around 2.1×10^{10} dyn cm^{-2}. As the film thickness increases, this value is gradually lowered to 8.2×10^9 dyn cm^{-2}. While the incremental film stress varies over the whole thickness range when the chromium film is deposited at room temperature it

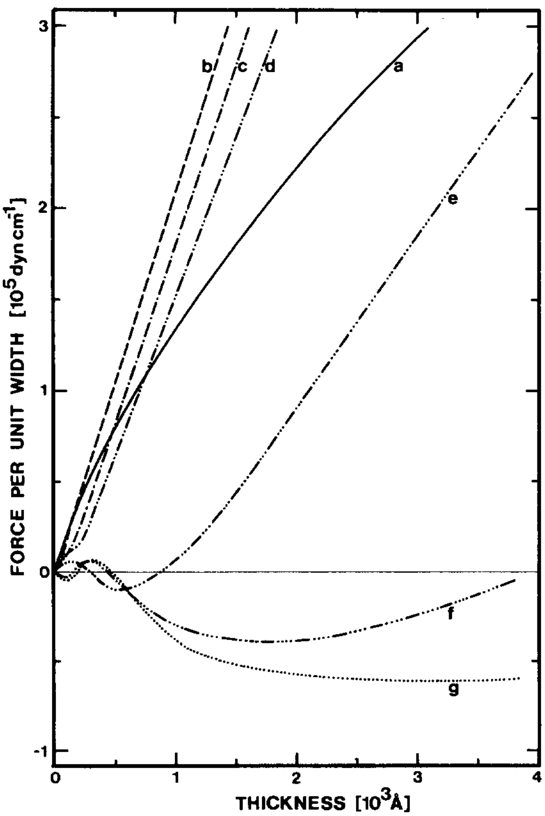

Fig. 2. Dependence of the internal stress of chromium films on the substrate temperature: curve a, 25 °C; curve b, 160 °C; curve c, 260 °C; curve d, 300 °C; curve e, 360 °C; curve f, 460 °C; curve g, 460 °C and a hydrogen partial pressure of 2×10^{-5} Torr.

maintains its value of 2.1×10^{10} dyn cm^{-2} when the film is deposited at a substrate temperature of 160 °C (Fig. 2, curve b). At a substrate temperature of 260 °C (Fig. 2, curve c) the initial incremental stress is reduced from 2.1×10^{10} to 7.6×10^9 dyn cm^{-2} in the thickness range 70–250 Å. Above 250 Å the incremental stress is again 1.9×10^{10} dyn cm^{-2} and remains constant. A similar trend is found at 300 °C (Fig. 2, curve d) where at a film thickness of about 80 Å the initial incremental stress of 2×10^{10} dyn cm^{-2} is lowered to 3.6×10^9 dyn cm^{-2}. For film thicknesses of more than 300 Å the constant stress is again 1.65×10^{10} dyn cm^{-2}. At 360 °C (Fig. 2, curve e) the initial incremental stress is 9.4×10^9 dyn cm^{-2}. At a mean thickness of about 40 Å a tensile stress maximum is observed with a force per unit width of 800 dyn cm^{-1}. As the film thickness increases the film stress becomes compressive and a maximum force of -9000 dyn cm^{-1} is reached at a mean thickness of 500 Å. For thicknesses above 500 Å the film stress is finally tensile with an incremental film stress of 9.2×10^9 dyn cm^{-2}. At 460 °C (Fig. 2, curve f) a compressive stress is built up in the film even during the early growth stage. Above 100 Å the internal film stress is again tensile with a maximum force per unit width of 6000 dyn cm^{-1} at a mean thickness of 260 Å. Then the film stress is once again compressive with a maximum force per unit width of -40000 dyn cm^{-1} at a mean thickness of 1700 Å. Beyond this thickness the internal stress of the chromium film is again tensile with an incremental stress of about 2.6×10^9 dyn cm^{-2}. This value represents the mean of three different experiments. The reproducibility of this final incremental film stress was not ideal since the interaction between the chromium and various components of the ambient atmosphere is not negligible at this temperature. Quadrupole mass analysis of the residual gas indicated that the primary component of the ambient gas was hydrogen produced during the evaporation of MgF_2. Curve g in Fig. 2 is a stress curve for chromium deposited again at a substrate temperature of 460 °C but at a partial hydrogen pressure of 2×10^{-5} Torr. The compressive as well as the tensile stress maxima at the beginning of the film growth are only very slightly affected. However, the second compressive stress maximum is shifted to a much higher mean thickness as a result of hydrogen uptake by the film.

4. DISCUSSION

In the past we have studied the internal stress of silver, copper and gold films as a function of the thickness and deposition parameters[11,12,14,16]. When these low melting point metals are deposited at room temperature a low compressive stress develops during the first growth stage. Then the film stress becomes tensile, and at the mean thickness at which coalescence of the previously isolated metal clusters is completed this tensile film stress reaches its maximum value. As the thickness of the continuous film increases the film stress again becomes compressive. Starting from this experimental evidence we have proposed a model for the origin of the internal stress of these metal films (refs. 11, 12 and references therein). According to this model three mechanisms can contribute a tensile stress: (i) surface tension as long as the film is still discontinuous; (ii) elimination of point defects, dislocations and grain boundaries; (iii) grain boundary relaxation. The compressive stress, however, we believe to be due to a compressive strain built up at the metal–substrate interface during the coalescence stage. At the end of the coalescence stage this interface strain reaches its maximum value. As the film thickness is then further increased we assume that this strain is communicated from the interface region through the whole film and therefore gives rise to a further compressive stress contribution (strain mechanism). From transmission electron microscopy experiments on the metals of the copper group we conclude that the film, viewed in cross section, consists of two parts: (i) because of the adhesion of the metal to the substrate, a structurally fairly stable interface layer; (ii) a second layer above this in which the film structure can change either during or after the deposition. In cases where these structural changes are slight, columnar growth is representative of the film growth, and the average grain size remains more or less constant as the film thickness increases. However, if the film material is mobile, recrystallization will take place either during or after the film deposition. Such a film viewed in cross section shows an increasing grain size from the interface to the vacuum side of the film. It should then be expected that the structure of the second layer influences the propagation of the strain field from the interface. In cases where, because of recrystallization processes, larger grains develop in the second layer we believe that this strain information is communicated through a thicker film than for films with a small average grain size. As discussed earlier[11] the size of the interface strain itself is influenced by the surface tension of the metal and the shape and adhesion of the metal clusters to the substrate. The mobility of the metal atoms on the substrate and on the metal itself therefore determines the magnitude of the compressive stress in the continuous film and the mean film thickness (*i.e.* the second compressive stress maximum) at which the strain information from the interface is lost. Above this thickness therefore the grain boundary relaxation mechanism is then the main remaining contribution to the film stress. Thus the thickness at which this compressive stress maximum appears and the incremental film stress beyond this thickness provide information about the extent of recrystallization and thus about the average grain size in the layer above the interface.

As already mentioned, the stress model summarized above was originally proposed to deal with experimental results obtained for low melting point metals (silver, copper and gold) with comparatively high mobility[8]. We have now intentionally chosen two materials, chromium and MgF_2, with higher melting points and thus distinctly lower mobility than the metals of the copper group. Although the stress curves differ considerably at room temperature we are demonstrating with this paper that, given comparable mobilities, the growth and internal stress properties of chromium and MgF_2 become very similar to those of the metals of the copper group at room temperature.

During the deposition of MgF_2 as well as of chromium at room temperature, only tensile film stresses are measured over the whole thickness range (Figs. 1 and 2). In terms of our stress model this indicates a predominant contribution of the grain boundary relaxation mechanism and thus, from the magnitude of the tensile stress, a rather small average grain size (see also ref. 5). In the case of the chromium stress *versus* thickness curve small changes in the incremental film stress suggest some recrystallization and thus increasing grain size during the initial growth stage. The incremental stress of MgF_2, however, remains constant over the whole thickness range. The gradually decreasing incremental film stress in chromium films thicker than about 300 Å (Fig. 2, curve a) we believe to be caused by either a partial slipping of the film at the chromium–substrate interface or the generation of microcracks in the film. Contrary to earlier work we now believe that this decreasing incremental film stress is not due to recrystallization processes or to interaction with the residual gases of the ambient atmosphere. Both the initial chromium film stress of 2.1×10^{10} dyn cm^{-2} and the MgF_2 film stress of 5.7×10^9 dyn cm^{-2} are slightly higher than previously reported values in the literature [2-6,8,9]. Differences in the cleanness of the substrates, which can affect the adhesion of the film to the glass beam may be the reason for the discrepancies.

The changes in the incremental stress of chromium films thicker than about 300 Å are eliminated as soon as the substrate temperature is increased. At 160 °C (Fig. 2, curve b) the film stress is constant over the whole thickness range. We interpret this to indicate that as a result of better adhesion between the substrate and the metal film at this temperature[17] the entire film stress is conveyed to the bending beam. At a substrate temperature of about 300 °C (Fig. 2, curve d) for the first time a distinct change in the incremental stress between 100 and 200 Å indicates a compressive stress contribution. The smaller incremental stress above 250 Å also indicates a slight reduction in the grain boundary relaxation contribution and thus a somewhat increased average grain size. At 360 °C (Fig. 2, curve e) the metal mobility is already sufficiently high that larger islands are formed during the initial growth stage. The tensile stress maximum at 140 Å then indicates the end of the coalescence stage. This delayed completion of the film coalescence manifests itself in a larger average grain size. This increase in grain size is also inferred from the fact that the incremental tensile stress beyond the compressive stress maximum at 500 Å is smaller. This trend is continued until at a substrate temperature of 460 °C (Fig. 2, curve f), because of the comparable mobility of the metals[8], the stress *versus* thickness curve is very similar to those published earlier for the metals of the copper group. Thus at higher substrate temperatures the mobility of the chromium is sufficiently increased that the influence of the grain boundary relaxation mechanism, dominant at lower temperatures, is reduced, and the other mechanisms which we believe to contribute to the total film stress are comparable in magnitude or even dominant at different stages of the film growth resulting in a sequence of compressive and tensile stresses. The compressive stress maximum in the continuous film is recorded at progressively higher film thickness and the final incremental tensile stress is gradually lowered as the substrate temperature is increased. In terms of our stress model these changes indicate that because of increasing recrystallization in the film at higher temperatures the average grain size increases and therefore the compressive strain built up at the substrate–metal interface during the coalescence stage is transmitted through progressively thicker films.

These interpretations of the stress *versus* thickness curves and the changes in these curves as the substrate temperature is increased are corroborated by the structure of the respective films visible in the transmission electron microscope. Figure 3 shows the micrographs of chromium films 290 Å thick at five different substrate temperatures. As can be seen the average grain size is indeed increased at higher substrate temperatures. This trend was also found by Imura[18] for substrate temperatures below 300 K. In agreement with the stress curves in Fig. 2 the increase in the average grain size is most pronounced at substrate temperatures above 300 °C. Figure 4 shows the electron microscope structure of chromium films

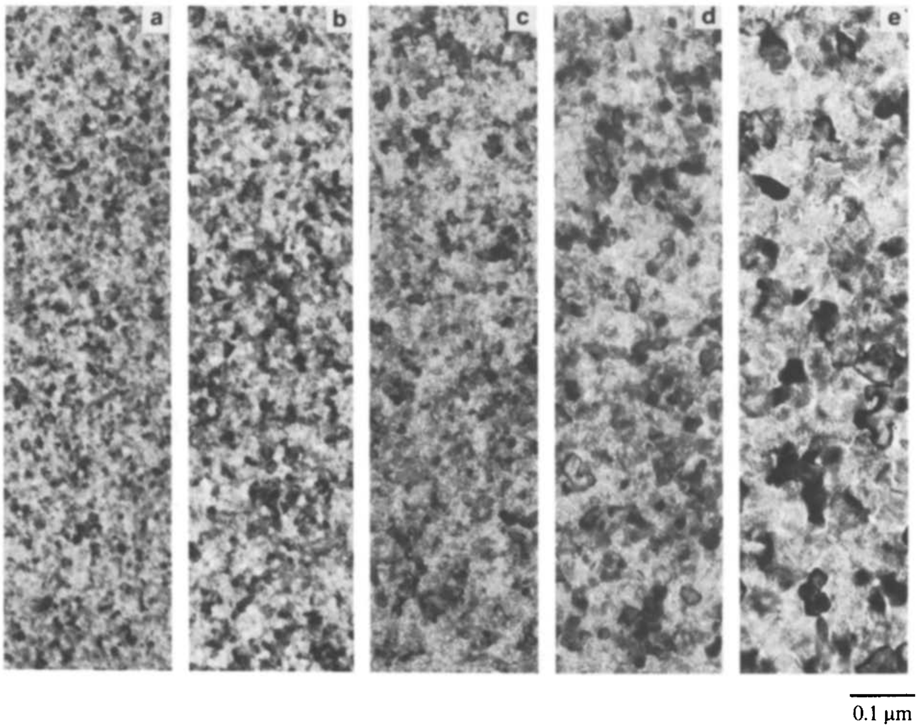

Fig. 3. Electron micrographs of chromium films 290 Å thick evaporated at different substrate temperatures: (a) 25 °C; (b) 160 °C; (c) 260 °C; (d) 360 °C; (e) 460 °C.

deposited at a substrate temperature of 460 °C as a function of the thickness. It is obvious, again as expected from the interpretation of the stress curve given above, that at a thickness of 150 Å (Fig. 4(a)) the chromium film is still discontinuous. At a thickness of 290 Å (Fig. 4(b)), slightly less than the thickness at which the tensile stress maximum occurs, a limited number of small holes and channels are still visible. The micrograph of a film 700 Å thick (Fig. 4(c)) shows the structure of a fully continuous film with an average grain size clearly larger than that at the end of the coalescence stage. Thus, at higher temperature firstly the coalescence of the chromium film is not complete to rather a high average film thickness and secondly the average grain size above the interface layer becomes larger as the film thickness increases. This increasing recrystallization at higher substrate temperatures is independently confirmed by the decreasing film resistivity which approaches the bulk value when the chromium films are evaporated at substrate temperatures above 300 °C. At room temperature, however, the high film resistivity indicates a small average grain size and thus columnar growth is representative of the growth of the film as a result of the low chromium mobility.

The internal stress of the MgF_2 film is only about half of that of the chromium film and the adhesion to the glass surface is sufficiently strong that the film stress is transmitted fully to the bending beam. The constant incremental film stress over the whole thickness range investigated ($d < 8000$ Å) again points towards columnar grain growth. While the incremental film stress agrees well with that reported by

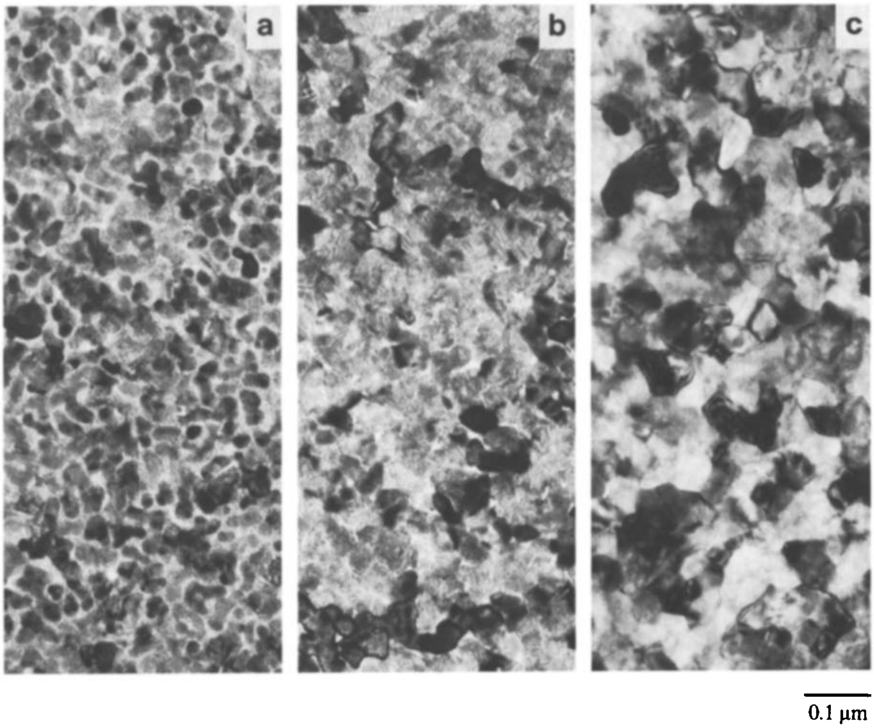

Fig. 4. Electron micrographs of chromium films of the following mean film thicknesses evaporated at a substrate temperature of 460 °C: (a) 150 Å; (b) 290 Å; (c) 700 Å.

Kinbara *et al.*[6] we did not observe the abrupt stress decrease at a mean thickness of 5500 Å, which may be because these researchers used a different substrate. Increasing the substrate temperature results in changes in the stress curve with similar trends as for chromium. However, while the final tensile incremental stress for chromium is not significantly changed up to a substrate temperature of about 300 °C it is already noticeably reduced at a considerably lower temperature in the case of MgF_2, a result also obtained by Kinbara *et al.*[6] The tensile stress maximum at a mean thickness of around 70 Å is again believed to indicate the end of the coalescence stage. While this maximum for chromium is shifted to a higher average thickness with increasing substrate temperature its position remains more or less constant for MgF_2. As in the case of chromium, however, the compressive stress maximum of the continuous film is shifted to a higher thickness as the substrate temperature is increased, again suggesting increasing reorientation in the film at higher temperatures and thus an increasing average grain size.

5. CONCLUSIONS

A bending beam apparatus was designed which allows the continuous determination of the internal stress of evaporated films at any substrate temperature up to 500 °C. With this device the internal film stress of chromium and MgF_2 films was measured as a function of the substrate temperature. At room temperature both materials exhibit only tensile stress over the whole thickness range. At higher substrate temperatures both compressive as well as tensile stresses are measured with increasing film thickness, similar to the stress curves of silver, copper and gold. For these metals, a model proposed previously for the origin of the internal stress is again applicable without limitations to interpret the changes in the stress curves of the chromium as well as the MgF_2 films with varying substrate temperature. These stress changes can be correlated with changes in the structure and therefore growth of the two films. The structures thus determined are in accord with the film structure visible in the electron microscope.

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