

The Effect of Thermal History on the Structure of Chemically and Vapor Deposited Silver Films on Glass

(Presented at Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems Conference, Lawrence Berkeley Laboratory, Berkeley, CA, July 28-30, 1980, and proposed for publication in Proceedings of Conference on Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems.)

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Prepared by Sandia Laboratories, Albuquerque, New Mexico 87115 and Livermore, California 94550 for the United States Department of Energy under Contract DE-AC04-76DP00789.

Printed September 1980

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SAND79-8825
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THE EFFECT OF THERMAL HISTORY ON THE STRUCTURE OF CHEMICALLY
AND VAPOR DEPOSITED SILVER FILMS ON GLASS

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ABSTRACT

The observation of silver agglomeration in second surface mirrors used for solar applications has emphasized consideration of the effect of thermal history on the optical properties of mirrors. Thermal history effects may arise from the processing of mirrors, the application of protective coatings, or from outdoor exposure. Mirrors may be subject to elevated temperatures ($T < 400^{\circ}\text{C}$) for short periods of time, or to low temperatures ($T < 60^{\circ}\text{C}$) for long (<30 years) periods of time. Although a significant amount of work has been done on thermally driven agglomeration of silver films, most of these studies have been restricted to vapor deposited films on vitreous silica. Large area reflectors, such as those used in heliostats, will almost certainly be deposited by commercial chemical methods on substrates of soda-lime-silicate or other glasses which differ considerably from vitreous silica in composition and properties. The present study addresses the effect of this change in deposition technique and substrate on silver agglomeration. These problems were studied by optical and scanning electron microscopy, reflectometry, and x-ray diffraction. The results indicate that both the method used to deposit the silver and the type of glass affect the agglomeration process and the character of the reflective film.

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CHEMICALLY AND VAPOR DEPOSITED SILVER FILMS ON GLASS

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INTRODUCTION

The observation¹ of silver agglomeration in second surface mirrors used for solar applications has emphasized consideration of the effect of thermal history on the optical properties of mirrors. Thermal history effects may arise from the processing of mirrors, the application of protective coatings, or from outdoor exposure. Mirrors may be subject to elevated temperatures ($T < 400^{\circ}\text{C}$) for short periods of time, or to low temperatures ($T < 60^{\circ}\text{C}$) for long (< 30 years) periods of time. Although a significant amount of work has been done on thermally driven agglomeration of silver films,²⁻⁷ most of these studies have been restricted to vapor deposited films on vitreous silica. Large area reflectors, such as those used in heliostats, will almost certainly be deposited by commercial chemical methods on substrates of soda-lime-silicate or other glasses which differ considerably from vitreous silica in composition and properties. The present study addresses the effect of this change in deposition technique and substrate on silver agglomeration. These problems were studied by optical and scanning electron microscopy, reflectometry, and x-ray diffraction. The results indicate that both the method used to deposit the silver and the type of glass affect the agglomeration process and the character of the reflective film.

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EXPERIMENTAL PROCEDURE

Vapor deposited films were prepared by a standard technique on vitreous silica and soda-lime-silicate glass substrates.⁸ Chemically deposited films were prepared by a commercial mirror manufacturer on a standard production line on both vitreous silica and commercial float glass. These "commercial" mirrors were coated with copper and paint over the silver. The paint was removed with glacial acetic acid and the copper was removed with ammonium persulfate before study.

The glass-film composites were heat treated in a controlled atmosphere furnace which was preheated to the desired temperature ($\pm 5^\circ\text{C}$) in 700 torr of the indicated gas. Vacuum treatments were made at a pressure below 10^{-7} torr.

The heat-treated samples were examined with a scanning electron microscope and by optical microscopy using both reflected and transmitted light. Specular reflectance measurements were made at 600 nm on a Cary 17I spectrophotometer equipped with a V-W specular reflectance accessory, and with a polychromatic (600 nm to 1100 nm peaking at 900 nm) portable specular reflectometer. The comparatively large beam size of the spectrophotometer sampled film areas of varying uniformity, whereas the smaller beam diameter (~ 1 mm) of the portable reflectometer enabled reflectance measurements to be made at a "point" in the film.

X-ray diffraction patterns were obtained from the thin films using a Diano XRD8000 system, and the data were reduced using a modified version of the Goehner program.⁹ Data were collected by point counting using times up to 500 seconds for some of the weaker peaks. Peak positions, intensities, and widths at half maximum were measured after the α_2 profile was stripped away.

RESULTS

Microscopy

Both chemically and vapor deposited silver films were agglomerated (Figure 1) after heating at 300°C in air for 30 minutes for both substrate glasses. A detailed examination of the effect of substrate composition and deposition technique on the appearance of heat treated films revealed that the agglomerated films on vitreous silica substrates were more uniform than those on the float glass substrates, and that the vapor deposited films were more uniformly agglomerated than were the chemically deposited films.

The chemically deposited films exhibited an unusual feature which was never observed in the vapor deposited films. The heat treated samples exhibited a number of areas of unagglomerated silver

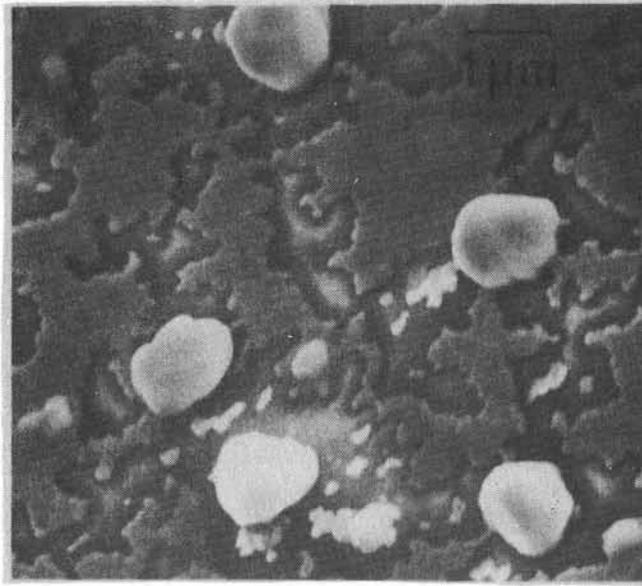


Fig. 1. Micrograph of agglomerated vapor deposited silver film.

which resembled comets, with a distinct "head" and a long, tapering "tail", as shown in Figure 2. The region in the center of the head was filled with agglomerated silver. EDX measurements during SEM analysis indicated that the comets frequently contained a region of high iron concentration in the smooth portion of the head region. It is possible that iron was introduced during the manufacturing process, because iron is used to reduce the copper in the deposition process.

Reflectance

The effect of temperature and atmosphere during heat treatment on the reflectance of chemically deposited silver films is given in Table I and shown in Figure 3. A sharp decrease in reflectance, which is indicative of sudden agglomeration, occurred at $\sim 300^{\circ}\text{C}$. As suggested by other authors,²⁻⁴ free oxygen must be presented for the agglomeration to occur. The presence of water vapor, or of other molecules containing oxygen, did not lead to agglomeration. A reduction in the partial pressure of air by a factor of ten reduced the degree of agglomeration, as indicated by the decreased effect on the reflectance. Heating in pure oxygen yielded a reflectance near that obtained by heating in air, but also resulted in a significantly less uniform agglomeration than did heating in air.

The effect of film thickness on agglomeration was studied for vapor deposited films ranging from 40 to 400 nm thick by heating at 300°C in air for one hour (Figure 4). The reflectance and the degree of agglomeration observed were about the same for films

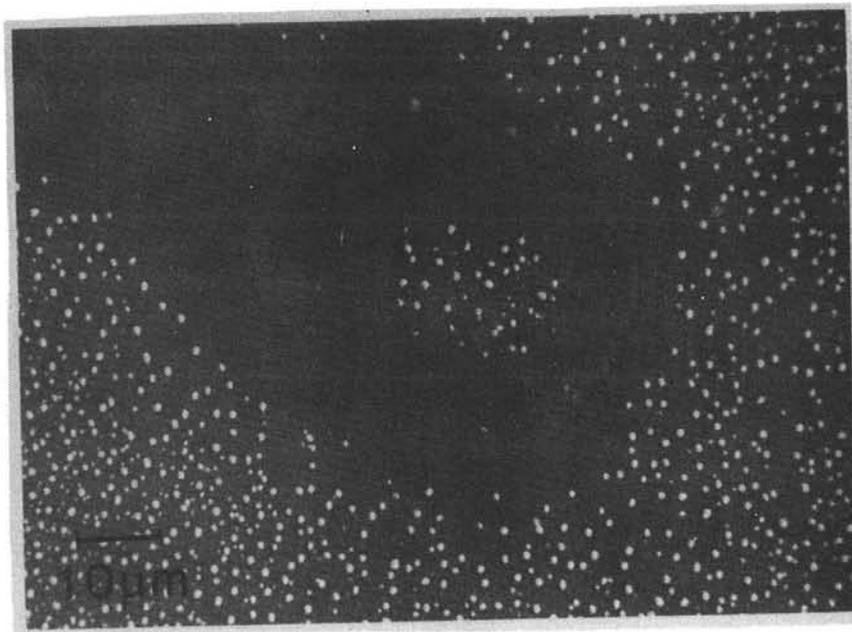
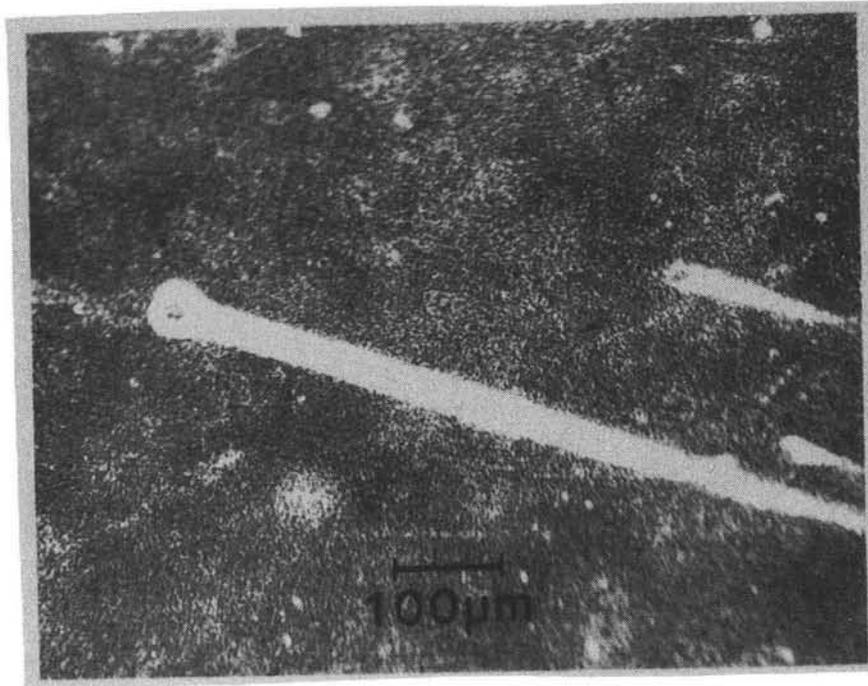


Fig. 2. Micrographs of heat treated (one hour at 300°C in air), chemically deposited silver films. The lower micrograph is an enlargement of the "head" of the comet shown in the upper micrograph.

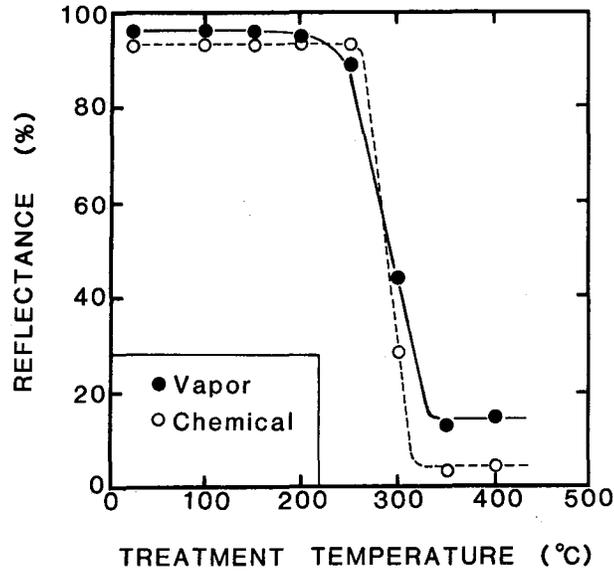


Fig. 3. Effect of temperature on the reflectance of silver films on float glass heat treated for one hour in air. (Measured at center point of sample by portable reflectometer.)

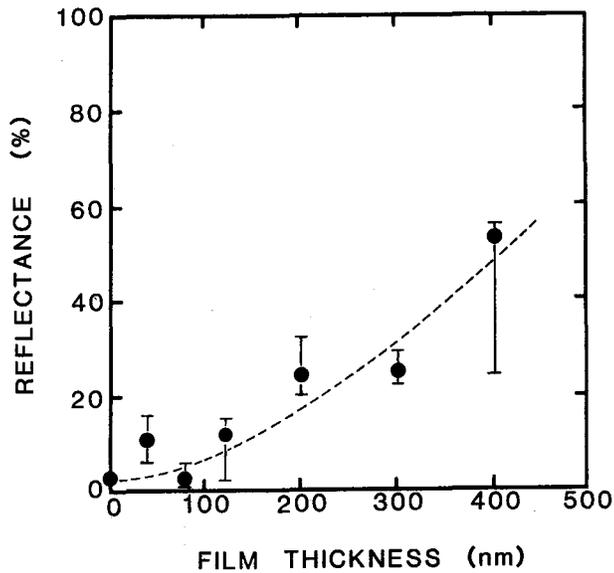


Fig. 4. Effect of film thickness on the reflectance of heat treated vapor deposited silver films on float glass. The points indicate the most common value measured, whereas the error bars indicate the range of values over the specimen area.

Table I. Effect of Thermal History and Atmosphere on the Reflectance at 600 nm of Chemically deposited Silver Films on Float Glass Substrates (Measured by Spectrophotometer).

<u>Atmosphere</u>	<u>Temperature (°C)</u>	<u>Pressure (torr)</u>	<u>Reflectance (%)</u>
Air	100	740	92
Air	150	740	90
Air	200	740	90
Air	250	740	72
Air	300	740	21
Air	400	740	15
Air	300	75	89
Vacuum	300	10 ⁻⁷	91
Vacuum	400	10 ⁻⁷	91
Hydrogen	300	700	89
Nitrogen	300	700	92
Nitrogen + Water	300	flowing	92
Nitrous Oxide	300	700	92
Methane	300	700	90
Carbon Dioxide	300	700	90
Oxygen	300	700	20-70

<80 nm thick. The thickest films (300 and 400 nm) exhibited a large degree of hillock formation and very rough surfaces, but did not appear to have any pinholes. The reflectance of the thinner films was essentially equal to that of the glass substrate (4%).

X-Ray Diffraction

Comparison of the diffraction traces of the as prepared chemically and vapor deposited films showed several distinct differences. Figure 5 shows this comparison for five of the measured peaks. The peaks intensities of the vapor deposited samples are much stronger and the width of the peaks are much narrower and better resolved in α_1, α_2 components, indicative of the greater size and perfection of the crystallites in these films. In addition, the ratios of intensities of many of these peaks are different from those obtained from a random powder, indicating the presence of preferred orientations. Table II lists the observed intensities for these first five diffraction lines compared with the pattern obtained from silver powder. The intensity ratios for the chemically deposited material are similar to the reference sample, but the vapor-deposited sample shows wide discrepancies, implying strong orientation with (111) lying in the plane of the film.

The differences in crystallinity between the two samples result in broad peaks for the chemically deposited films and only slightly broadened peaks, relative to these same films after complete

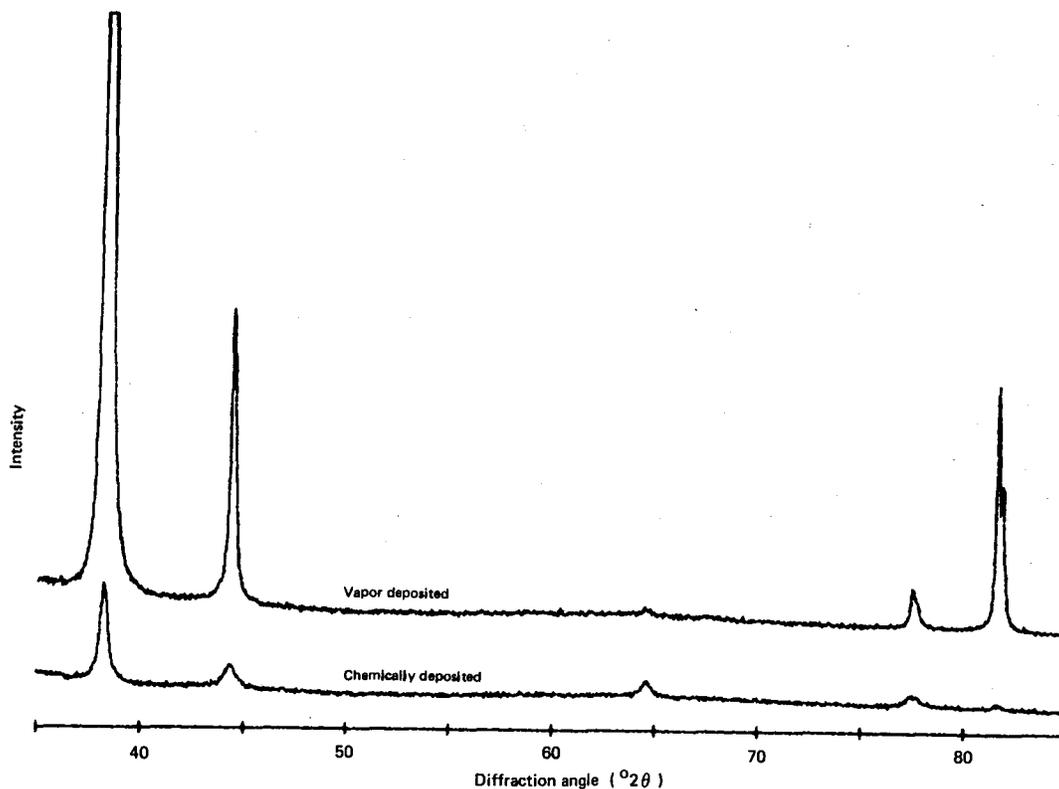


Fig. 5. Diffraction patterns obtained from annealed vapor and chemically deposited silver films showing differences in crystallinity and preferred orientation.

Table II. Relative-absolute Peak Intensities for Vapor and Chemically Deposited Silver Films Obtained from Unannealed and Annealed Films Compared with Reference Values for Bulk Silver.

Material	hkl				
	(111)	(200)	(220)	(311)	(222)
Chemically deposited unannealed	46	11	5	5	1
Chemically deposited annealed at 400°C	100	41	19	17	4
Vapor deposited unannealed	2395	144	0	22	145
Vapor deposited annealed at 400°C	2873	111	0	12	120
Bulk silver (4-783)	100	40	25	26	12

annealing, for the vapor deposited films. Representative profiles are shown in Figure 6. Thermal treatment results in sharper peaks, primarily due to increases in crystallite size and perfection. The very broad profile obtained from the unannealed, chemically deposited sample (Figure 6A and Table II) shows considerable sharpening and a marked increase in peak intensity when annealed at 400°C. Much smaller changes are observed when the vapor deposited films are annealed (Figure 6B and Table II). The annealing increases the peak intensity of both types of films but has essentially no effect on the orientation. It should also be noted that there is no shift of peak position with annealing, implying no change in lattice parameters occurs. Lattice parameters based on the (333) reflection yield a value of $4.0848 \pm 0.0002 \text{ \AA}$ for all of the vapor deposited films and were independent of the annealing temperature. This value is to be compared with the value of 4.08651 \AA obtained on annealed silver powder.¹⁰

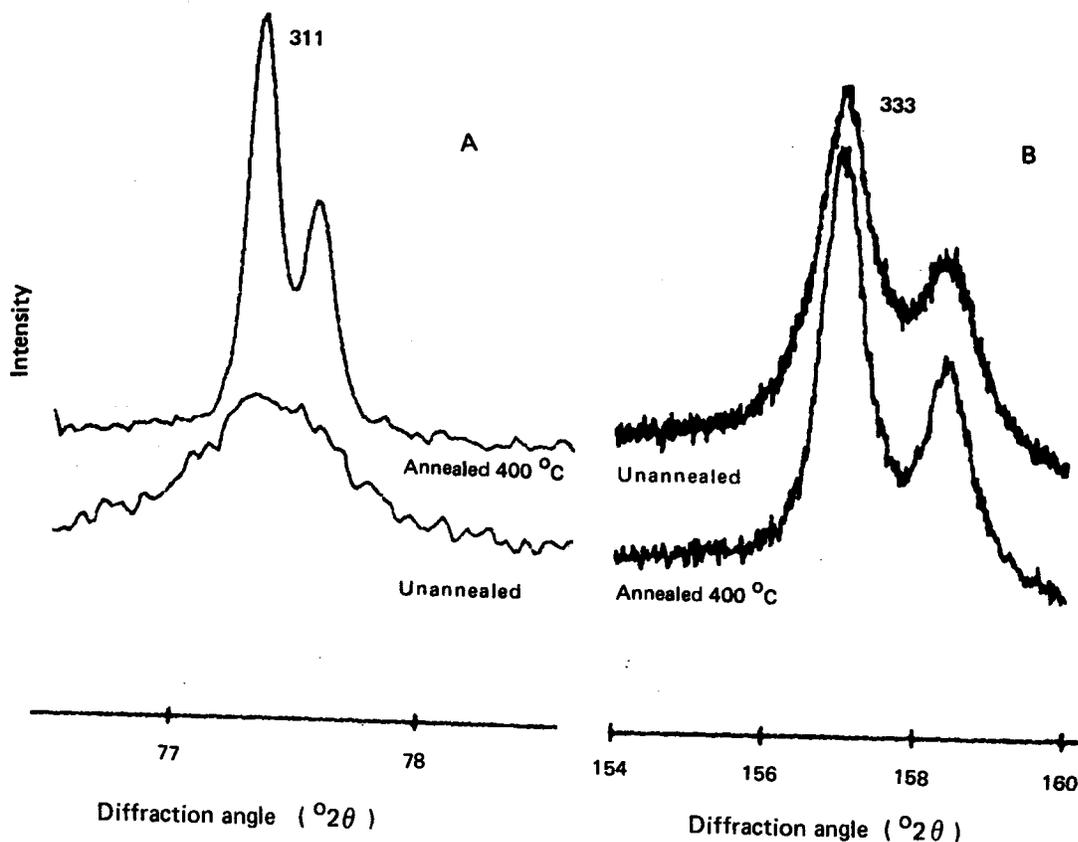


Fig. 6. Diffraction traces of (A) the 311 line from chemically deposited silver films and (B) the 333 line from vapor deposited silver films showing the changes which occur with annealing at 400°C.

Figure 7 shows the behavior of the line profiles as a function of annealing temperatures for both types of films. The half width of the profile is sensitive to crystallite size, defect concentration, and strain. The detailed Warren-Averbach type of analysis necessary to separate these effects was not performed in this study. For comparison among the samples, an apparent crystallite size has been used which is the size implied from the peak width assuming no broadening is due to defect or strain. The vapor deposited films (Figure 7A) show a slight trend to narrower peaks with temperature, with the largest changes occurring around 300-350°C. The (111) and (222) profiles are distinctly narrower than the (200) and (311) profiles. The initial apparent crystallite sizes are in the 1000 Å range for (200/311) and at least twice this value for (111/222). In the chemically deposited samples (Figure 7B), the apparent crystallite sizes are approximately 400 Å as measured using the (111/220/222) reflections and 200 Å when the (200/311) peaks are used. The chemically deposited films show continuing decreases in broadening with annealing above 100°C, and the distinctions between the different profiles disappear above 300°C. Apparent crystallite sizes above 300°C are >1000 Å. The similarity of behavior of (220) to (111) and (222) is what would be expected if (111) twin boundaries or stacking faults were present in the crystallites because one-half the (220) planes remain coherent across the twin interface or stacking fault. The apparent 2:1 size ratio indicated by (111/220/222) and (200/311) half widths suggests an average of one twin or stacking fault per crystallite.

It should be noted that the major changes in crystallinity occur over roughly the same temperature range as does the agglomeration. The increase in mobility of silver which results in the agglomeration also results in grain growth. This grain growth eliminates some of the defects in the chemically deposited films as indicated by the similarity in widths between (111/220/222) and (200/311) profiles. However, this grain growth does not result in any change in lattice constant for either the chemically or vapor deposited films.

CONCLUSIONS

The results of this study indicate that there are significant differences between the structures of chemically and vapor deposited silver films on float glass substrates. The vapor deposited films exhibit a strong preferred orientation effect which is absent in the chemically deposited films. The apparent crystallite size in the chemically deposited films is initially much smaller than that of the vapor deposited films, but it gradually increases with heat treatment temperature until it reaches that of the vapor deposited films at ~350°C. The crystallite size in the vapor deposited films is only slightly

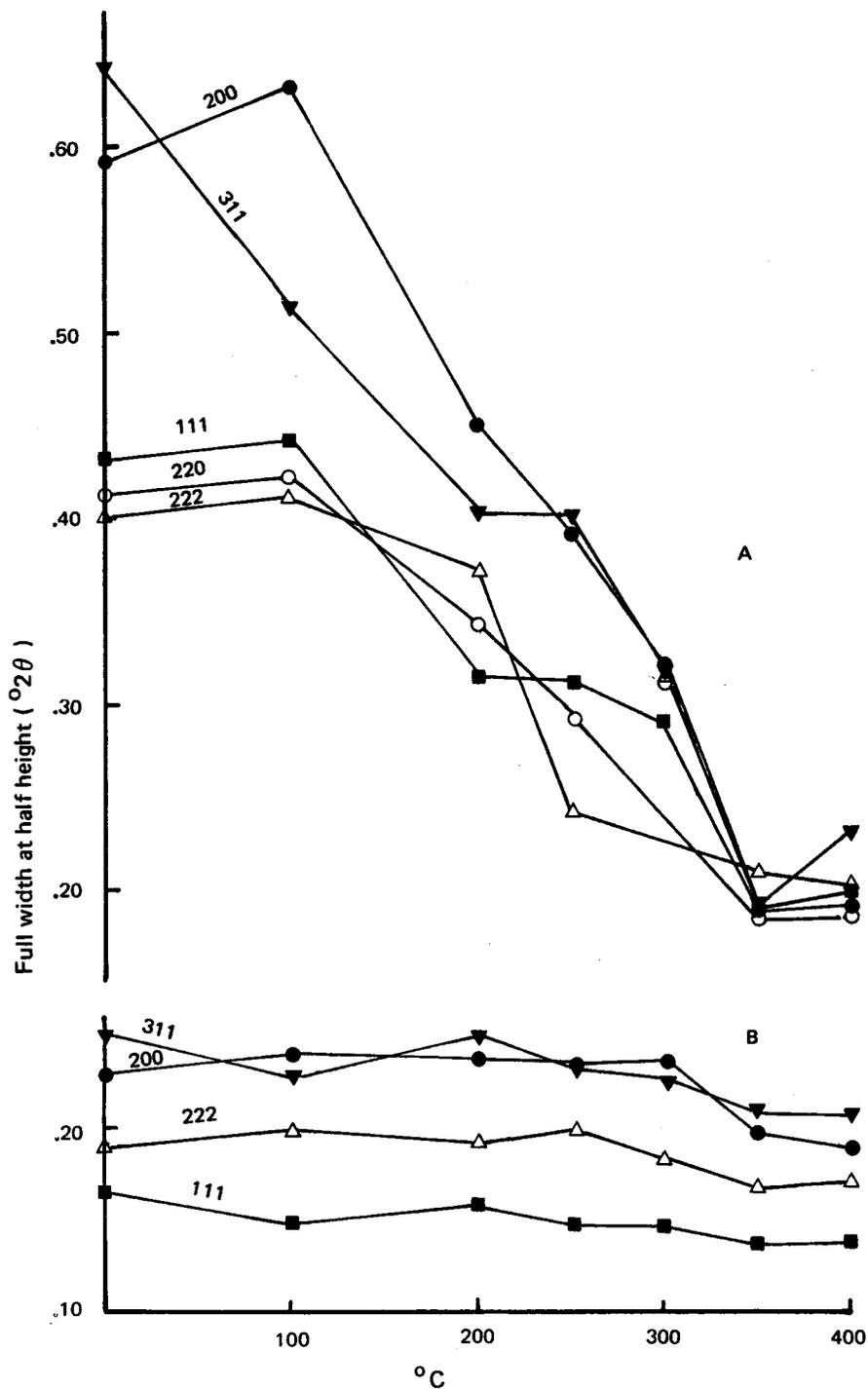


Fig. 7. Variation of half widths of diffraction profiles from (A) vapor deposited and (B) chemically deposited silver films with annealing.

increased by temperature. The crystallite orientation of both chemically and vapor deposited films is unaffected by thermal annealing. Microscopic observations indicate that the chemically and vapor deposited films both exhibit silver agglomeration above 200°C. The vapor deposited films appear to be more uniform in structure than the chemically deposited films, and the chemically deposited films exhibit the unusual feature described as "comets" which probably results from impurities introduced during manufacturing. It is evident from this study that previous work dealing with vapor deposited silver films on vitreous silica may not be unequivocally applied to chemically deposited silver films on other glasses.

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ACKNOWLEDGMENT

Experimental measurements were made by W. L. Smith, R. D. Gay, C. Karfs, and D. Boehme.

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