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Stress in Alkali Halide Films

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A detailed investigation has been made of the stress in alkali halide films evaporated onto glass, and it has been shown that this can be done satisfactorily by measuring the end deflection of a substrate using a surface probe. Initial difficulties arising from residual stress in the substrates have been largely overcome by carefully annealing the glass. The stress has been derived from the curve of observed deflection, plotted in terms of the force factor, against film thickness.

A survey of the various models for explaining stress has been made and it has been shown that there are at least two, different, stress-producing mechanisms. In the early stages of growth, a misfit model is suggested, in which the oxygen sites in the glass surface act as preferred positions for the metal ions of the halide. The situation is not as clear in thicker films, but either a thermal expansion or a density model could provide a partial explanation.

1. Introduction

It has long since been established that many electrodeposited films are in a state of tensile stress (see, for example, references 1 and 2). Similar stresses have been observed in metal films deposited by vacuum evaporation [3-5] and evidence indicating that some dielectric films are deposited in compressive stress has also been published [6-10]. Information on the stress in evaporated films is useful to enable manufacturers to fabricate stable thin-film circuits, for, in extreme cases, tensile stress can lead to cracking, and compressive stress to buckling of the circuit elements. However, there is some evidence that a certain amount of compressive stress in both electrodeposited [11] and evaporated films [12] is advantageous for stabilising the layers.

The objects of the work reported here were to continue earlier measurements on dielectric films [13] in greater detail and to examine the possible causes of intrinsic stress, particularly in the initial stages of growth. By *intrinsic stress* is meant the stress remaining in the film after an allowance is made for all the thermally induced stresses. It seemed likely that more useful information would be obtained by limiting the study to a relatively small group of materials with similar structures, rather than by examining a large number of entirely different films. The alkali halides suited this requirement and had the additional advantage that evaporations could be made with the source at relatively low temperatures. Glass substrates were used throughout. Some measurements have also been made on mica, but these are not considered here.

2. Basic Methods

Although stress can be deduced in principle from changes in the lattice parameters of the films, calculated from X-ray [14, 15] or electron diffraction [16] patterns, the method is rather complicated and very careful measurements are required. Consequently, most workers have made direct observations of the bending of thin substrates caused by deposition of the film. This method is simple to apply, and highly sensitive techniques for measuring the curvature of the substrate have been developed.

Generally, the stress is calculated from the end deflection of a cantilevered substrate in the form of a strip of rectangular section. The relationship between the average stress, S, and the

end deflection, Δ, was first given by Stoney [17] and later discussed in more detail by Brenner and Senderoff [18], viz.

$$S = \frac{\Delta E_S t_S^2}{3L^2 t_f} \qquad (1)$$

where E_S is the Young's modulus of the substrate, t_S and t_f are the thicknesses of substrate and film respectively, and L is the length of the film.

In deriving the equation, it is assumed that the film thickness is much smaller than that of the substrate (this is always true in practice), and that the elastic moduli of the film and substrate are equal. Davidenkov [19] has considered the case of unequal moduli, but has obtained an expression in integral form which can only be solved numerically. However, it is shown fairly easily that, even when the moduli differ by an order of magnitude, the correction needed is very small for practical values of t_S and t_f. Hoffman [20] has indicated that significant errors in the stress values may be introduced if the substrate dimensions are such that the width of the substrate is more than half the length, or the deflection Δ is greater than the thickness t_S.

Hoar and Arrowsmith [21] have pointed out that the stress is biaxial and not uniaxial as assumed in the above derivations, and Davidenkov has shown that the difference can be taken into account by multiplying the stress value obtained from equation 1 by the factor $1/(1 - \nu)$; where ν is the Poisson ratio of the substrate. In most previous work this factor has been neglected.

The formula is derived by making the assumption that both the film and the substrate are homogeneous and isotropic. This will not always be the case, as it is known that an island type of growth often occurs in very thin films [22, 23]. In these circumstances, the average film thickness is used in the stress equation, and the stress value obtained will differ from that existing in the individual crystallite. Furthermore, in evaluating the stress, it is tacitly assumed that no slip occurs between the film and substrate. This assumption is reasonable for stress values up to $\sim 5 \times 10^9$ dyne/cm^2, if the adhesion energy exceeds 5 kcal/mole. However, more data on adhesion is needed before a categorical appraisal can be made in specific cases.

As mentioned earlier, several different techniques have been used to measure the free-end deflection of the cantilever. These methods have been discussed by Campbell [24] and by Hoffman [20], who have examined the relative sensitivities by comparing the minimum stress observable in a film 1000 Å thick. Although this definition is useful for illustrative purposes, it is worth noting that it can be misleading unless stresses in films deposited on substrates of similar dimensions are compared. On the basis of the above definition, methods in which the end deflection is sensed by a transducer in contact with the substrate seem to be most sensitive, with a minimum detectable value $\sim 10^6$ dyne/cm^2. However, it would be difficult to make measurements on substrates at elevated temperatures by these methods, owing to problems associated with the thermal isolation of the detector. For this type of measurement, the capacitance method used in recent work by Wilcock [25] or the interferometric method described by Ennos [10], both of which have sensitivities approaching that of the mechanical methods, would be more suitable.

However, measurements of the stress in alkali halide films were not envisaged with the substrates above room temperature, and the Talysurf probe method [13] seemed to be the most suitable. One disadvantage was that the probe itself could not be baked and, as this had to be used within the vacuum chamber, system pressures were limited to about 10^{-5} torr.

3. Experimental

3.1. Apparatus

The system used for making the measurements is shown in fig. 1 and is basically a refinement of the one used earlier [13]. The pumping unit is an optically baffled, 4 in., oil-diffusion pump. The halide under investigation is evaporated from a directly heated, molybdenum crucible, which is nearly enclosed by a water-cooled heat shield. A camera shutter, which is shielded from the evaporant during preliminary outgassing, is introduced into the main vapour stream to enable the shorter evaporation times to be more accurately defined. Additional baffles are provided between the source and substrate; these tend to define the evaporant stream and lessen the possibility of scattered material from reaching the substrate, while at the same time reducing the stray thermal radiation. The reverse side of the substrate is protected from extraneous deposition by a baffle fixed about 1 mm away

from it. The distance between the source and substrate is about 25 cm.

The Talysurf probe and a special jig holding the substrate are mounted on a brass plate which forms the upper part of the vacuum chamber. A permanent magnet is used to clamp the substrate to the jig, which is designed to allow the

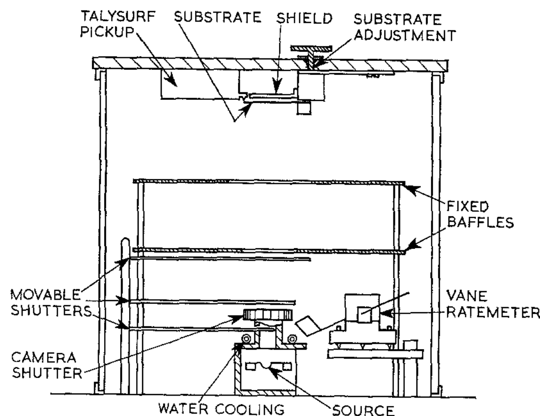

Figure 1 Diagram of system used for stress measurements.

free end of the substrate to be moved relative to the diamond probe of the Talysurf from outside the vacuum chamber. This enables the pen position on the output recorder to be adjusted. A continuous record of the end deflection is obtained on the chart, and a second pen, activated by the camera shutter, is used to mark the exposure time.

An accurately balanced vane ratemeter [26], situated about 3 cm from the source, allows rates down to 0.5 Å/sec to be set up.

3.2. Thermal Effects

The deflection, observed during deposition of the film, is the resultant of the deflections arising from intrinsic stress and from thermal expansions in the substrate and film. These expansions can possibly originate from the bulk temperature rise, when the substrate is not homogeneous and isotropic, from the temperature gradient across the substrate, and from differential expansions between the substrate and film. The thermal flux incident on the substrate originates from source radiation and latent heat carried by the incident evaporant stream. As the actual temperature distribution developed during condensation of the film is dependent on so many factors (e.g. substrate and film materials, deposition rate, geometry of the system), it is only possible to measure it experimentally or to make an estimate for the idealised cases. For alkali halide films deposited on glass substrates, the overall temperature gradient is unlikely to exceed 0.1° C [13], whilst experiments indicate that the bulk temperature rise is typically ~10° C. However, owing to variations in the substrate properties, even a knowledge of the temperature distribution would be insufficient to enable the thermal expansion contribution to be determined.

The difficulty can be partially overcome by cutting down the thermal deflection as much as possible. A step in this direction can be taken by reducing the stray radiation with heat shielding. However, the latent heat still gives rise to a significant deflection. In principle, the thermal component can be eliminated by allowing the substrate to cool before measuring the deflection, but it is still possible for changes in the intrinsic stress to occur during this period. In alkali halide films, these changes could be caused by absorption of water vapour from the vacuum system or by relaxation processes. Significant changes caused by differential contraction between the film and substrate are unlikely to occur. Hoffman [27] has indicated that surface temperatures of ~700° C can be realised only momentarily (~10^{-12} sec), as each atom is deposited, and would be very localised in the film surface. Stress changes, produced by cooling from the observed temperatures during deposition (~10° C rise), are at least an order of magnitude less than the actual stress values.

It has been assumed throughout the experimental work that no changes in the intrinsic stress occur after deposition of the film. The film has been allowed to cool before measuring the end deflection to eliminate thermal effects; a standard cooling period of 3 min has been used. As indicated below, this is sufficient to allow most of the thermal deflection to disappear.

3.3. Substrate Annealing

The initial experiments were made by exposing the soda-glass substrates (~4 × 2.25 × 0.015 cm), used in the stress measurements, to radiation from a hot empty crucible and monitoring the end deflection. It was observed that the movement was not always away from the source, as would be expected from differential expansion considerations. Furthermore, there was a net deflection on cooling, which was occasionally as much as 50% of that produced during heating.

It was established that this residual deflection arose mainly from strain in the glass, and could be removed by very careful annealing (570° C for ½ h followed by a slow cool at < 15° C/h down to 480° C). After this treatment, the residual deflection was generally less than 10% of the total movement after a cooling period of 3 min. Even after annealing, end deflections toward the source were observed. These were attributed to the inhomogeneous nature of glass.

3.4. Technique

Prior to annealing, the glass substrates were ultrasonically cleaned in baths of distilled water, to which a little Teepol had been added, and isopropyl alcohol. Evaporations were not normally commenced until the system pressure was below 3×10^{-5} torr. During evaporation, the gauge was switched off to avoid possible modifications to the growth caused by electric charge [28]. The Talysurf pen was adjusted to a convenient position on the output chart, the recorder switched on, and the reading noted. The charge was outgassed for half a minute, the predetermined rate was set up by adjusting the crucible temperature, and the substrate exposed to the evaporant. After the evaporation, as previously mentioned, 3 min were allowed to elapse, then the net deflection was measured. In typical experiments, the net deflection changed by a third during cooling. Net deflections towards the source were interpreted as tensile stresses. The film thickness was generally measured directly in the thicker films above 200 to 300 Å with the Talysurf [26]. For thinner films, this was not feasible, and the thickness was deduced from the time and the ratemeter calibration.

As indicated by equation 1, Young's modulus was required, and this was found by adding a series of known weights at a fixed position along the substrate and measuring the resultant deflections. These measurements were made before the substrate was removed from the stress jig. The average thickness was determined from the weight of the substrate.

3.5. Accuracy

The relationship between the Young's modulus and the observed end deflection δ is

$$E_S = \frac{2WL^2(3L - l)}{\omega \delta t_S^3} \tag{2}$$

where l, the distance from the support at which weights W are added, and ω, the width of the substrate, are the additional symbols. A correction can be applied to allow for the change in cross-section on bending, but this involves ν^2 and is very small. Hence E_S can be determined from the slope, m, of the straight line obtained by plotting δ against W.

Substituting this value in equation 1 gives

$$S = \left\{\frac{2(3L - l)}{3(1 - \nu)}\right\} \frac{\Delta}{m t_S t_f} \tag{3}$$

The bracketed term contains quantities which are invariant. Consequently, the error in their measurement, which is of the order of 5%, affects only the absolute stress value. The accuracy with which Δ can be determined is difficult to estimate, as it depends on the deflection of the Talysurf recorder pen. Typically, the deflection is about a centimetre and therefore the error is ±5%. The error involved in determining m is also likely to be of this order. The substrate thickness is not uniform, and it is estimated that the absolute measurement of thickness is only to within ±3%. The deposited films are uniform, so that the error involved is merely associated with the measurement. In most films, the thickness can only be found with the Talysurf to within ±50 Å, so there is a ±5% error in measuring a 1000 Å film with a proportionately greater error in thinner films. For very thin films, a direct measurement is insufficiently accurate, and the thickness is estimated from the ratemeter calibration and the deposition time. In these cases, the accuracy is determined primarily by the constancy of the rate during deposition. At high rates, control of the evaporation is difficult and more significant errors are likely to be introduced.

Consequently, apart from the errors introduced by irreversible expansions in the substrate, the error in measuring the absolute stress value in a 100 Å film is probably ~±20%. Moreover, the errors will be significantly larger in thinner films. When the stress is plotted against film thickness, there is a possible error of at least ±5% along the thickness axis. Thus, in presenting the stress in this form, the errors in film-thickness measurement are reproduced in both axes. A better way of analysing the experimental data is to derive the stress curve from a plot of deflection against thickness. In this work, the deflection is not plotted directly, but the force

factor, F, defined by equation 4, is used instead.

$$F = \frac{\Delta}{mt_S} \quad (4)$$

The factor F takes into account the most significant variations in substrate properties. In some cases, a correction has to be applied to F. The force exerted by the Talysurf probe on the substrate is a function of position: this variation is linear and therefore can be defined by a force gradient. An analysis shows that this force variation can lead to significant errors in the measurement of F. However, providing that the deflections measured in the Young's modulus and stress experiments are both in the same direction, the error in one measurement is counterbalanced by an equal error in the other. When this condition cannot be fulfilled, a correction involving the force gradient and the slope m can be applied to each force-factor value.

The stress at any film thickness is simply proportional to the slope of the line joining the point on the force-factor curve to the origin.

4. Results

The experimental data are plotted in terms of the factor F, from which the average stress in the film has then been derived. The convention has been adopted of plotting parameters corresponding to tensile stresses in the positive direction.

4.1. Lithium Fluoride

Evaporations were carried out at 10 and 60 Å/sec. The deflections were towards the source and indicated a tensile stress (fig. 2a). The stress in films thicker than about 100 Å is substantially independent of thickness (fig. 2b). Deposition rate has very little effect; the tendency is for the stress to be larger at the higher rate.

4.2. Other Lithium Halides

No detailed measurements were made on the other lithium halides. At deposition rates of 15 Å/sec, the stress was tensile both in a 1100 Å thick film of lithium chloride and in a 600 Å thick film of lithium bromide. A thin film (~170 Å) of lithium bromide gave a nearly zero value of stress.

4.3. Sodium Fluoride

At a deposition rate of 15 Å/sec, there is a large scatter in the experimental values for film thicknesses above 200 Å and the force-factor curve cannot be well defined (fig. 3a).

The stress curve for the early stages of film growth has a markedly different form from the other alkali halides. The initial stress is tensile with a maximum $\sim 6 \times 10^8$ dyne/cm^2 at about

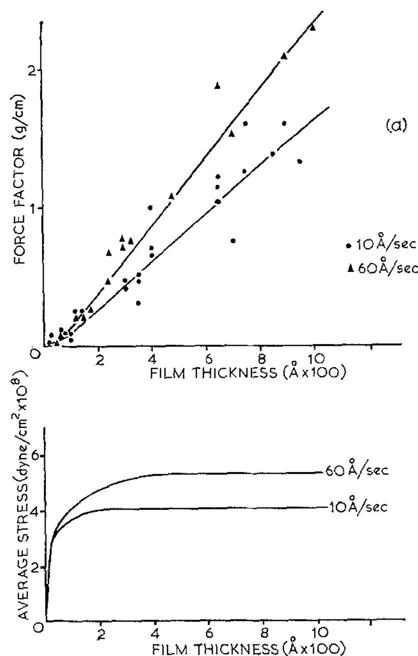

Figure 2 Stress behaviour of lithium fluoride films: (a) force-factor curves; (b) stress curves.

20 Å thickness (fig. 3b). As the film gets thicker, the stress changes to compressive at about 60 Å thickness, and a maximum $\sim 5 \times 10^8$ dyne/cm^2 occurs at 100 Å. The subsequent behaviour has not been definitely established, but it seems likely that the stress remains compressive at least up to 1000 Å thickness.

4.4. Sodium Chloride

Two deposition rates, 15 and 50 Å/sec, were used. The force-factor curves (fig. 4a) are well defined by the experimental points. The stress is compressive in films thinner than about 900 Å, with a maximum $\sim 4 \times 10^8$ dyne/cm^2 occurring at about 200 Å (fig. 4b). The effect of deposition rate is not significant.

4.5. Sodium Bromide

The behaviour is similar to that of sodium chloride. At a deposition rate of 20 Å/sec, the force-factor curve (fig. 5a) is well defined. The stress is compressive in films thinner than about

700 Å, and a maximum $\sim 3 \times 10^8$ dyne/cm^2 occurs at about 200 Å (fig. 5b).

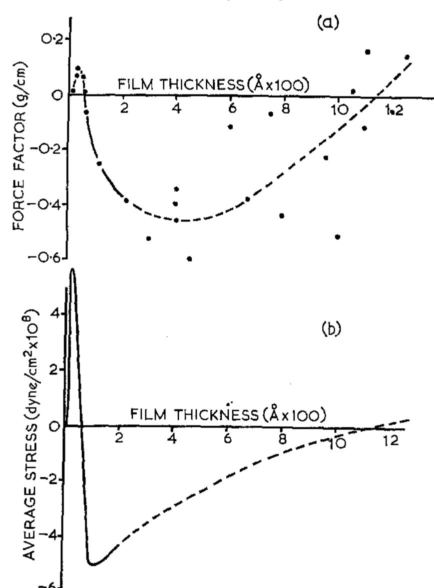

Figure 3 Stress behaviour of sodium fluoride films (deposited at 15 Å/sec): (a) force-factor curve; (b) stress curve.

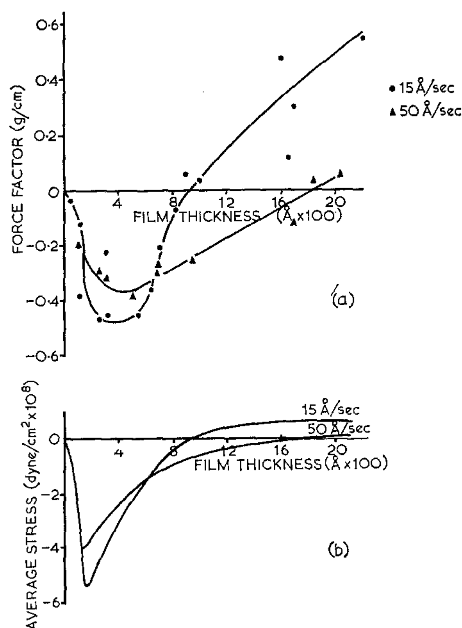

Figure 4 Stress behaviour of sodium chloride films: (a) force-factor curves; (b) stress curves.

4.6. Potassium Fluoride

Detailed measurements were not made. The values of stress calculated from three experiments made at a deposition rate of 15 Å/sec are shown in table I.

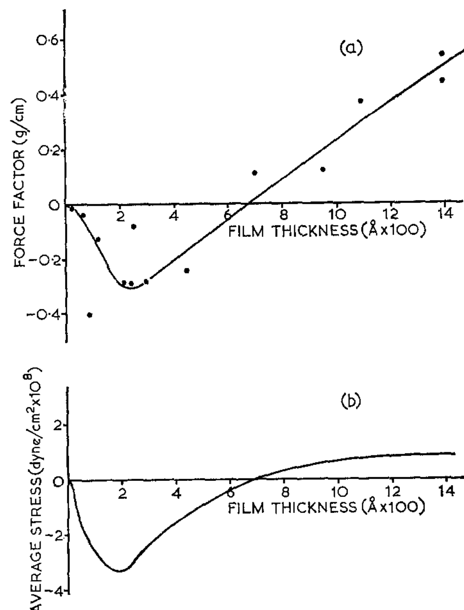

Figure 5 Stress behaviour of sodium bromide films (deposited at 20 Å/sec): (a) force-factor curve; (b) stress curve.

TABLE I Stress in potassium fluoride.

Thickness (Å)	Stress (dyne/cm^2 $\times 10^8$)
270	Not detectable
540	−3.4
1500	+1.1

These suggest that the form of the stress curve is probably similar to that of sodium bromide.

4.7. Potassium Chloride

Results were obtained at deposition rates of 5, 30, and 60 Å/sec. All the deflections (fig. 6a) correspond to a compressive stress and show a relatively small scatter. The stress curves (fig. 6b) have a maximum $\sim 5 \times 10^8$ dyne/cm^2 at about 250 Å and there are no pronounced effects arising from the different deposition rates.

4.8. Potassium Bromide

All the deflections (fig. 7a) at a deposition rate of 15 Å/sec correspond to a compressive stress. The stress curve (fig. 7b) has a maximum $\sim 4 \times 10^8$ dyne/cm^2 at about 200 Å. The general form is similar to that of potassium chloride.

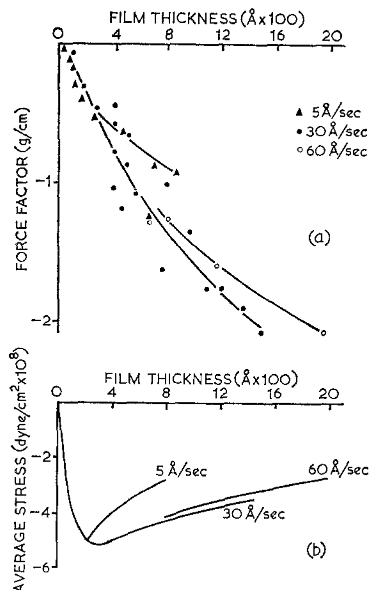

Figure 6 Stress behaviour of potassium chloride films: (a) force-factor curves; (b) stress curves.

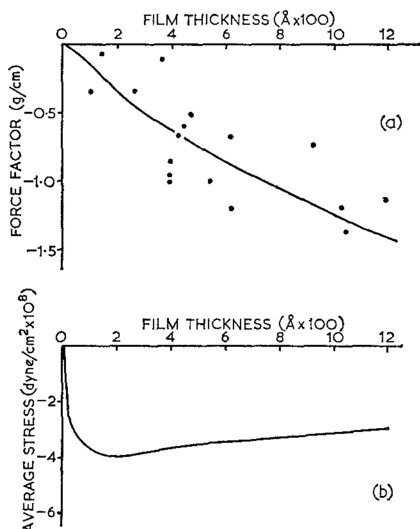

Figure 7 Stress behaviour of potassium bromide films (deposited at 15 Å/sec): (a) force-factor curve; (b) stress curve.

4.9. Potassium Iodide

Although experiments were made at several deposition rates, the data are insufficient for rate curves to be drawn. Instead, an average curve is given (fig. 8a). The stress is always compressive in thin films (fig. 8b), and a maximum $\sim 4 \times 10^8$ dyne/cm^2 occurs at about 300 Å. The general form is similar to that of the potassium halides.

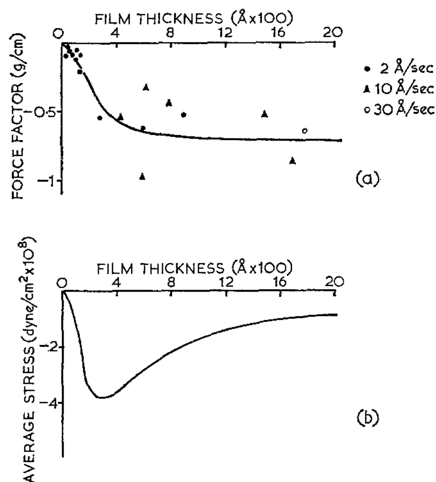

Figure 8 Stress behaviour of potassium iodide films: (a) force-factor curve; (b) stress curve.

4.10. Rubidium Iodide

No recent data are available, although early experiments indicated that the stress is compressive in films up to 1200 Å thick and rates between 20 and 100 Å/sec. However, the end deflections were measured within a few seconds of the end of the evaporation and included a thermal component.

4.11. Summary of Observations

The stress curves given above have some features in common.

(*a*) A stress maximum, which is usually compressive, tends to occur at a film thickness of about 200 Å.

(*b*) A constant stress is developed in films thicker than 1000 Å. In sodium and lithium halides this is tensile.

(*c*) The stress values are always less than 6×10^8 dyne/cm^2.

(*d*) The deposition rate has very little effect on stress.

The stress curve for sodium fluoride is exceptional, as it exhibits an initial tensile stress in films thinner than $\sim$60 Å.

5. Electron Microscopy Studies

Several different halides (lithium fluoride, sodium fluoride, sodium chloride, potassium bromide, rubidium iodide) were evaporated onto carbon

grids in a specially designed microscopy stage, which fitted in place of the air lock on the Siemens Elmiskopp I. This type of experiment has been described before [29] and is essential to avoid recrystallisation effects with the alkali halides [30]. However, it proved to be very difficult to obtain reasonable micrographs. The structures observed were generally badly defined and very low in contrast. Furthermore, they were easily modified by the action of the electron beam [23].

In the case of lithium fluoride, in which the effect of recrystallisation is believed to be small, there was very little similarity between the films deposited on carbon in the microscope and those obtained earlier by evaporation in a separate system [23].

Owing to these difficulties, detailed investigations of the structures of the alkali halide films could not be carried out.

6. Discussion

An examination of the curves shows that in some cases the experimental scatter is far greater than that expected from the errors discussed in section 3.5. The reasons for these variations are unknown, although a very broad scatter is also shown in other comparable papers on stress [9, 31]. As in the present work, the stress was obtained from measurements made on a large number of different films and not merely from the examination of a single film.

No independent measurements of stress in alkali halide films have been made previously and all the evidence, to which reference will be made later, is indirect. The results reported earlier on lithium fluoride [13] indicated a tensile stress with a maximum of $\sim 10^9$ dyne/cm^2 at about 200 Å thickness and a substantially constant stress in films thicker than 600 Å. The stress seemed to increase as the deposition rate was increased. However, as the measurements were made shortly after deposition had ceased, a thermal component arising from the overall temperature rise would have been included. In addition, the Poisson ratio correction was not applied.

In a typical alkali halide film, there appear to to be two, different, stress-producing mechanisms, one predominating in thin films of up to about 200 Å thick, and the other becoming significant in thicker films. It is tempting to correlate these two mechanisms with the growth onto the substrate and onto the film-coated substrate respectively. However, the available evidence on the structure of alkali halides, which has not been substantiated by the observations with the electron microscope detailed earlier, suggests that a film of 100 Å is substantially continuous. It is possible that the stress maximum actually occurs in much thinner films and that its position has been altered by the rather artificial definition of stress used for this region.

6.1. Initial Stress

6.1.1. Misfit Model

Considering the initial stages of growth in which deposition is primarily onto the glass substrate, fig. 9 shows the stress in 50 Å films of the various halides plotted as a function of the corresponding lattice spacings. A straight line can be drawn through the experimental values cutting the axis at about 5.3 Å. The values have been taken at a thickness of 50 Å, since at this thickness the deposition is still primarily onto the substrate itself, and the measurements are reasonably reliable. With the exception of sodium fluoride, values chosen at any other thicknesses up to 100 Å fit on the same type of straight line, giving an intercept around 5.3 Å. Above 100 Å, there is no regularity of the type shown in fig. 9.

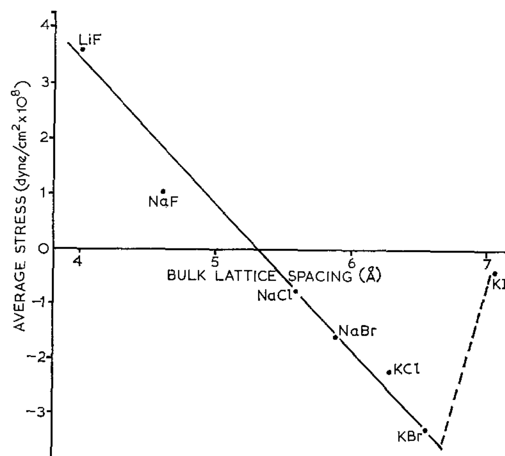

Figure 9 Average stress in 50 Å films of various alkali halides plotted against lattice spacing.

A model with this type of characteristic has been proposed by Van der Merwe [32] for oriented films on single-crystal substrates. It was shown that the minimum energy state in thin films with small misfits was one in which elastic deformation of the film took place until the lattices were matched. This concept may be

useful for describing the stress in polycrystalline films deposited on polycrystalline or amorphous substrates.

In glass, the structure can only be defined in terms of the most probable spacings between atoms, which can be obtained from a radial distribution analysis of the diffraction pattern [33]. The surface structure is predominantly that of silica, in which the next nearest-neighbour distance between oxygen atoms is 5.3 Å. Consequently, if the most probable spacings for the glass are taken as representing the lattice spacings in a real crystallite, the observations can be fitted to a Van der Merwe type of model when the halides are in (100) orientation and the surface sites are oxygen atoms. Evidence for the existence of a (100) fibre orientation has been obtained by Schulz [34] for the cases of LiF and NaCl (< 100 Å) on amorphous substrates. The lattice spacings in the films would have a distribution about 5.3 Å. So far, no diffraction measurements have been carried out on alkali halide films of this thickness, although Grigson and Dove [35] have recently shown that, in the case of nickel-iron films deposited on carbon, an amorphous film with a distribution of lattice spacings is formed initially. The assumption that the surface sites are the oxygen atoms seems reasonable, as oxygen is negatively charged [36] and the bond would form through the positive metal ions in the film. One other difference between the curve and Van der Merwe's model is the existence of a linear stress-strain relationship at much higher misfits than the 12% value calculated theoretically as the maximum possible. Fig. 9 indicates that the linear relationship is true for misfits up to at least 25%, although there is a distinct possibility that in the case of potassium iodide (misfit ~33%) the relation is no longer linear. However, the original model was based on the concept of a fit for every atom. In the present case, the fit need only occur over a small proportion of surface atoms. This view is supported by calculations of strain energy in the films which give values less than 10% of those expected on Van der Merwe's model under critical misfit conditions.

The spot measurements on potassium fluoride ($d = 5.33$ Å) and lithium bromide ($d = 5.49$ Å) indicated zero stress in the thinnest films and are therefore consistent with the model.

6.1.2. Lattice Spacing Model

In the case of the alkali halides, it has also been suggested that the stress arises from the difference between the lattice spacings of bulk material and small crystallites [5]. If the lattice spacing of the crystallite is smaller than that of bulk, the interior atoms will be in compressive stress, while a larger-than-bulk spacing would lead to a tensile stress.

Several attempts have been made to measure the lattice constants of alkali halide films by electron diffraction. For several alkali halide films, including lithium fluoride, Boswell [37] found that the spacings were all less than that of bulk. Subsequently, Rymer [16] pointed out that these conclusions were not necessarily correct, as the usual theory of electron diffraction was not applicable to the crystallites smaller than about 50 Å diameter. Larger crystallites of lithium fluoride were examined by Halliday *et al* [38] and a larger-than-bulk spacing was observed. However, in the cases of sodium and potassium chlorides, the spacings seemed to be identical to the bulk material [39]. In more recent work, Mcrae [40] obtained a larger-than-bulk spacing for lithium fluoride and Marklund [41] found a similar result for sodium chloride.

Consequently, the balance of these results from diffraction studies would indicate that the stress in lithium fluoride should be tensile, as is found in practice. The diffraction studies on sodium chloride are contradictory, but would lead to either a zero or a tensile stress on the lattice spacing model. However, the observed stress is compressive.

The smaller- and larger-than-bulk spacings can also be considered as equivalent to positive and negative surface tensions respectively. Several authors have calculated the surface tension in the (100) faces of alkali halides having the NaCl structure by estimating the various interatomic binding forces. The earliest calculation was made by Lennard-Jones [42], who considered an isolated plane of atoms and obtained positive values for the surface tension. Subsequently, the effects of the different layers were taken into account. Shuttleworth [43] calculated that in all sodium and potassium halides, with the exception of sodium fluoride, the surface tension was negative. The general trend of his results suggested that the lithium halides should have positive values. A more recent calculation by Nicolson [44] gave positive values for all the alkali halides, in agreement with the conclusions reached in later work by Benson [45]. However, considerable differences occur in the magnitudes

of the surface tensions predicted by these authors. Hence, the two most recent, theoretical papers predict that the stress should be compressive in all alkali halides. This is not in agreement with the stress observed in lithium fluoride films.

It is evident that there are anomalies which cannot be reconciled at present, and, before the validity of the surface tension models can be established, more results of lattice spacing measurements on thin films are needed.

At the present time, it is not possible to explain the linear stress-lattice spacing relation given in fig. 9 in terms of surface tension.

6.2. Stress in Thicker Films

6.2.1. Thermal Model

The situation occurring in thicker films has not been examined in great detail. One possible model, first suggested in relation to nickel films by Murbach [46], depends on the contraction of the film on cooling from the recrystallisation temperature. This explanation has been discussed by several authors [27, 47, 48], and it has been pointed out that the high temperature could be developed only momentarily and very locally on arrival of each incident atom. In addition, the observation that the stress could be altered by annealing to a temperature above that of deposition but below that of recrystallisation could not be explained. The temperature effects have been considered theoretically by Gafner [49], but the compressive stress in gallium [50] does not fit into this analysis.

Similar difficulties are encountered when a thermal model is applied to explain stress in dielectric films, although as the magnitudes of the stresses are less than in metal films, the film temperature does not need to be as high. The compressive stress observed in most alkali halides is not necessarily a limitation: the stress curves have been plotted in terms of average rather than instantaneous stress and can be somewhat misleading. For example, when the operative mechanism is producing a tensile stress, the average stress may still appear to be compressive after an initially compressive stress has been introduced into the film. However, the general trend in the stress curves suggests that a tensile stress would be developed in all cases providing that the films are sufficiently thick.

6.2.2. Density Model

A model proposed by Buckel [51] depends on the densities of solid and liquid phases of the film material. It is stated by Ostwald's Rule that the liquid phase must be present during condensation of the film. Provided that this liquid phase is considered to be bound to the underlayers, a tensile stress would be developed on condensation when the solid is denser than the liquid. The model has had some success in predicting the compressive stress in gallium films [50], but the stress in antimony films [52] is tensile even though the liquid is denser than the solid. Information on the densities of all the alkali halides at their melting point is not available. Although both sodium and potassium chlorides have a solid phase denser than the liquid [53] leading to a tensile stress, the expected stress would be at least an order of magnitude greater than actually observed.

7. Conclusions

The measurement of the end deflection of the cantilevered substrate with the Talysurf probe has been found to be a suitable means for determining the stress in alkali halide films. Initial difficulties arising from residual stress in the glass substrates have been largely overcome by careful annealing of the glass. The thermal stress component has been eliminated by allowing a relatively long cooling period to elapse before making measurements, although the assumption that the intrinsic stress does not alter during this period has had to be made. The stress has been derived from the curve of observed deflection, plotted in terms of the force factor, against thickness.

The pattern of the results suggests that there are at least two, different, stress-producing mechanisms in alkali halide films. In the early stages of growth, a misfit model seems most likely, although an explanation in terms of surface tension has been considered also. More data on the lattice spacings in the surfaces of alkali halides are needed for justification of a surface tension model. The position in thicker films has not been examined so critically, but it seems that either a thermal expansion or a density type of model could provide a partial explanation.

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