NDL-TR-106

THE INFLUENCE OF SUBSTRATE TEMPERATURE ON THE STICKING COEFFICIENT OF ZINC ON GLASS

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ABSTRACT

The influence of glass substrate temperature between room temperature and 95° C on the sticking coefficient of zinc-on-glass in a vacuum of 10^{-6} torr was studied. The sticking coefficient was found to be significantly higher at 65 to 95° C. At room temperature no adsorption of zinc was observed even after the glass surface was exposed to a high flux of zinc vapor atoms for 15 minutes.

Contamination effects on the sticking coefficient are described; it was noted that at temperatures within the range of 65 to 95° C a uniform and continuous film of zinc deposited on glass slides cleaned with nitric acid and water. The effect of change in the flux of the zinc vapor on the sticking coefficient is also discussed. Three theories are proposed to explain the phenomena of increased sticking of zinc with increased substrate temperature.

FOREWORD

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CONTENTS

THE INFLUENCE OF SUBSTRATE TEMPERATURE
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1. INTRODUCTION

When a molecule in the vapor state strikes a solid surface, it either rebounds or sticks. The probability of its sticking, the condensation coefficient, is difficult to predict because of its dependence on a number of physical properties and experimental parameters. These include the nature and temperature of the substrate, the nature of the vapor, the flux or frequency of the vapor atoms hitting the substrate, the composition of the adsorbed surface film of the substrate, and the pressure at which the deposition occurs (i.e., the extent of contamination of the vapor beam and the substrate surface by residual gas atoms).

The effect of these parameters on the deposition of gaseous metal atoms has been studied in a number of instances. The results are reported and discussed in terms of either the sticking coefficient or the condensation coefficient. The condensation coefficient is the probability of retention of a gaseous molecule by a surface with which it collides, whereas the sticking coefficient is an experimental value equal to the fraction of impinging molecules retained by a surface during the course of a deposition. If the reevaporation rate of deposited atoms is significant, the sticking coefficient will be less than the condensation coefficient.

Much of this work that has been completed in the last 30 years has been reviewed by Wexler (Reference 1). It has been experimentally established that the elements of Group I-b, silver, gold, and copper, have sticking coefficients approaching unity regardless of the surface. Devienne (Reference 2), for example, reports that the sticking coefficient for gold on glass, copper, or aluminum is 0.90 to 0.99. The elements of Group II-b, cadmium, zinc, and mercury, however, act in a much less predictable manner, with sticking coefficients that are dependent on the chemical nature of the substrate as well as on the composition of the adsorbed gaseous layer. Knudsen (Reference 3), Wood (Reference 4), and Devienne (Reference 5), report very small sticking coefficients for cadmium on glass or metal, whereas Garin and Prugne (Reference 6) report a sticking coefficient of near unity for cadmium on an aluminum surface that has been freshly deposited under vacuum. Wessel (Reference 7) showed that for zinc-on-zinc the sticking coefficient is unity, whereas according to Garin and Prugne (Reference 6), the sticking coefficient of zinc on an aluminum surface prepared in vacuum was zero.

Subsequent investigations showed that one of the determining factors for nucleation, in addition to the chemical nature of the substrate, was the condition of the substrate surface and its treatment prior to

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deposition of the zinc, cadmium, or mercury atoms. Fray and Nielson (Reference 8) demonstrated the importance of surface treatment by comparing the adsorption of zinc on fresh glass and on glass that had not been freshly melted and recooled. They found that fresh glass, according to electron micrographs, was free from surface imperfections and had a lower sticking coefficient than glass with pits and scratches on its surface. They observed in the electron micrographs taken of both surfaces that the vapor nucleated preferentially on the surface imperfections such as the scratches and pits. Preferential nucleation was further reported by Yeh and Siegel (Reference 9) and Wells and Siegel (Reference 10) who noted that condensation of cadmium and silver on mica occurred on the discontinuities of the mica.

In addition to the physical nature of the surface, the influence of surface contamination on nucleation was studied by many investigators. It was reasoned that impurity effects were likely to decrease the number of possible nucleation sites on the substrate and, therefore, increase the likelihood of reflection of an incident atom. Fray and Nielson (Reference 8) found experimental evidence that agreed with this reasoning when they noted that the sticking coefficient of zinc on glass was reduced if the glass surface was first "poisoned" by hydrocarbons. Yang, et al. (Reference 11), observed that the sticking coefficient increased with the increasing deposit thickness on glass and reasoned that as the thickness of the adsorbed layer increased, the impurity in the layers decreased. Devienne (Reference 5) confirmed this evidence when he noted that the sticking coefficient increased sharply with the thickness of the built-up deposit. Devienne, therefore, concluded that the nature of the substrate surface is fairly important during the first 20 Å of a condensed layer when the deposition is predominantly heterogeneous, i.e., the vapor atoms are striking a surface of different composition from the vapor atoms. After this, the original substrate layer is relatively unimportant; deposition has progressed to a homogeneous stage where vapor atoms are depositing onto condensed vapor atoms. Devienne reasoned that deposition onto thick layers is analogous to deposition on freshly formed surfaces that are free from contamination.

All of the experiments described above were carried out in what is now known as a low vacuum, i.e., 10^{-5} to 10^{-6} torr. It was not until the development of high vacuum techniques, which could produce pressures of 10^{-9} torr and lower, that nucleation studies on clean surfaces could begin. It has been calculated by Hirth, Hruska, and Pound (Reference 12) that surfaces in low vacuum were actually being contaminated by the residual gases in the system at a rate of one monolayer per second. Using high vacuum techniques, Garin and Prugne (Reference 6) cleaned a glass substrate by gas discharge and found that the sticking coefficient of cadmium on this clean surface approached unity, whereas values much less than unity were obtained by Devienne (Reference 5) for cadmium on glass in low vacuum. Chirigos, et al. (Reference 13), studied the nucleation of silver on polycrystalline copper in high vacuum (10^{-10} torr) and in low vacuum (10^{-6} torr) and reported that the nucleation rate was much lower for the low vacuum. They attributed this difference to surface contamination. Ptushinskii (Reference 14) applied this approach to a system of silver on molybdenum and reported a sticking coefficient of 0.9 at low vacuum compared with 1.0 for the same system at high vacuum. His findings were in agreement with Chirigos, et al.

An equally important factor that influences the efficiency of nucleation is substrate temperature. It was noted that, for a particular beam and surface material, there is a substrate temperature above which no permanent deposit was formed. For silver on glass this temperature is over 575° C, as reported by Knudsen (Reference 3), Gerlach and Stern (Reference 15), and Stern (Reference 16). Critical temperatures far below room temperatures were observed for cadmium and mercury by early workers. For cadmium on glass, the critical temperature was found to range from -140° C, according to Knudsen (Reference 3), to -50° C, as reported by Eastermann (Reference 17). The influence of the surface preparation on the critical temperature is also noticeable in the case of mercury on glass where values of -140° C to -130° C were obtained by Knudsen (Reference 3), and by Seddig and Haase (Reference 18) for mercury on chemically cleaned glass; this is opposed to the critical temperature of 20° C obtained by Seddig and Haase (Reference 18) for mercury on glass cleaned and baked at 450° C. Knudsen (Reference 3), with the use of mercury, zinc, cadmium, magnesium, copper, and silver, and Wood (Reference 19), who worked with mercury, iodine, and cadmium, carried out experiments in which partial pressures of the various materials were established over glass substrates containing temperature gradients. They found that a critical temperature existed above which no condensation occurred even if the beam flux were varied. Chariton and Semmenoff (Reference 20) also used a gradient substrate temperature technique and found a critical temperature for condensation of cadmium on paraffin, mica, and picein, but suggested that the critical temperature varied slightly with change in beam flux.

Frauenfelder (Reference 21), however, could find no critical temperature for beams of zinc, cadmium, and mercury on clean metallic surfaces even when the temperature was raised to 250° C. Gen, et al. (Reference 22) contended that there was no critical temperature above which there was no permanent nucleation. Instead, they reported that deposition was observed above the designated critical temperature after long periods of substrate bombardment.

Devienne (Reference 2) reported a decrease in the probability of antimony and gold sticking on glass when the surface temperature is raised above 25° C. This decrease in the sticking coefficient with time is attributed by Wexler (Reference 1) to be a result of a film on the surface. He affirms that above 150° C the film on the surface is absent and there is no decrease in the sticking coefficient with time. Supporting this concept that accompanying the increase in substrate temperature there is a reduction in impurity effects, Cockcroft (Reference 23) found that at 103° C the sticking coefficient was the same for cadmium on copper as for cadmium on silver or glass. He proposed that this was the result of a clean surface common to all three types of substrate rather than the result of variances in temperature. Frauenfelder (Reference 21) maintained, nonetheless, that the sticking coefficient has little dependence on temperature between 20 and 200° C for cadmium, silver, copper, or mercury. Studies made by Sears and Hudson (Reference 24) on the condensation of zinc vapor on glass, and by Rapp, Hirth, and Pound (Reference 25) on the condensation of cadmium and zinc on glass, gave no indication of a significant temperature dependence of the sticking coefficient of zinc.

One aspect of the nucleation of zinc that has been given notice, particularly in the literature of the past few years, concerns the critical supersaturation of zinc vapor; that is, the critical flux of vapor atoms necessary to bring about condensation on a solid surface. Whether the temperature of the zinc migrating on the substrate surface is at the temperature of the substrate, or is actually at a temperature intermediate to that of the substrate and the vapor atoms, has been a theoretical question long discussed in the writings of many investigators. Sears and Cahn (Reference 26) and Sears and Hudson (Reference 24) have proposed a theory which fits their experimental data and conforms with the classical theories of nucleation presented by Langmuir (Reference 27) and Frenkel (Reference 28). Shade (Reference 29) has challenged this theory and has experimentally demonstrated that nucleation is not dependent on both beam flux and vapor temperature. Shade concludes that the thermal relaxation time experienced by an adsorbed atom when it impinges on a surface is very short when compared with the residence time of an atom on the surface (i.e., the time spent by the atom on the surface before reevaporation or condensation to a stable nucleus). The controversy as to the real temperature of the adatom becomes even more confused when it is noted that Shade was considering a system of cadmium on polystyrene, whereas Sears, Cahn, and Hudson were studying zinc on glass. Although it might be expected that the activity of zinc and cadmium vapor atoms are similar because of their positions in the periodic table, it is clear that the nucleation properties of zinc are different from those of cadmium. In addition, there is strong possibility of different relaxation times on polystyrene as opposed to glass.

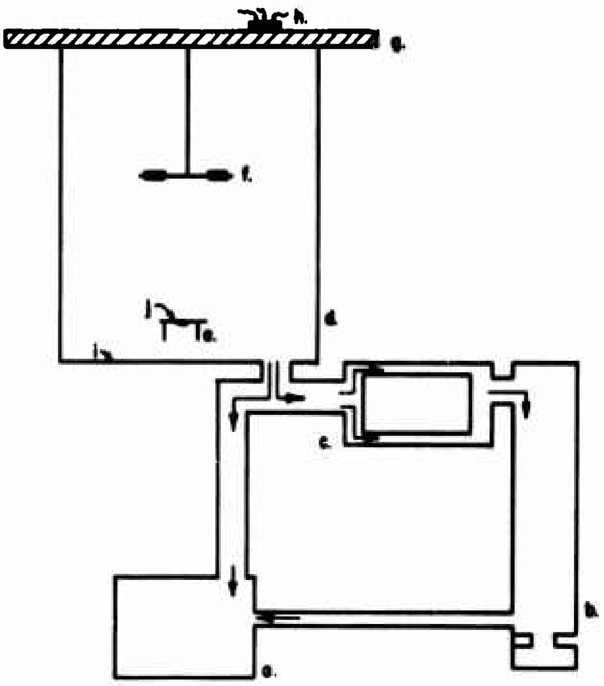
Conflicting studies have also been reported on the effects of substrate temperature on the nucleation of metal atoms. Some reports are incomplete and frequently the descriptions of surface preparation have not been included. There is also a great variety of vacuum conditions employed, which make comparison of results almost impossible.

This study further examines the influence of the glass substrate temperature on the sticking coefficient of zinc, and the influence of vapor flux and surface contamination on the sticking coefficient.

2. PROCEDURE

2.1 Apparatus.

The experimental system, Figure 2.1, consisted of an electrically heated boat to vaporize the zinc, glass slides to be used as target substrates, and wire heaters placed against the glass slides to produce the desired substrate temperatures. The system was enclosed in a vacuum chamber. During the experiments the residual gas pressure was always less than 10^{-6} torr.



a. rotary forepump
b. diffusion pump
c. cold trap
d. vacuum chamber
e. electrode

f. target assembly
g. upper base plate
h. wire leads
i. lower base plate
j. molybdenum boat

Figure 2.1 Experimental System.

The vacuum system consisted of a 75 ℓ min^{-1} rotary forepump (a) and a 2-inch diameter diffusion pump (b) connected in series and separated from the vacuum chamber by a liquid nitrogen cold trap (c). Before each experiment the chamber was cleaned with dilute Alconox solution and distilled water. The vacuum chamber was pumped down to 10^{-8} torr, filled with helium, and reevacuated. This was repeated three times to remove most of the air from the system.

Zinc, 99.999 percent pure, was heated to vaporization in a molybdenum boat positioned on the base plate inside the vacuum chamber. The boat (j) was held 2 inches above the base plate (i) by two metal electrodes (e).

Ordinary lime glass microscope slides were used as the target substrate. Tests were also conducted with Corning substrate glass*, and Vycor (quartz). Two techniques for cleaning the glass slides were employed. By the first method, the glass slides were soaked in fresh hot potassium dichromate cleaning solution from 2 to 5 minutes, followed by a number of rinses in distilled water, and then dried with Kimwipes. By the second method, the slides were washed in a warm solution of Alconox and rinsed in distilled water for 1/2 hour. The slides were then soaked in concentrated nitric acid for at least 1/2 hour, washed with distilled water, and dried with Kimwipes. The slides were carefully positioned in metal slide holders, thermocouples were affixed to the center of the test slides, and the apparatus was placed in the vacuum chamber.

The glass samples were positioned horizontally 10 inches above the beam source. The slides were then heated by electrical wire heaters positioned between two of the target slides (Figure 2.2). The heaters consisted of B&S #28 nichrome wire wound around the glass slides twenty-five times. A variation of this type heater in which the bare wires were covered with Sauereisen was also tested. Before each experiment, the slides were heated for a period from 2 hours to 3 days at temperatures to 100° C to outgas any adsorbed gases or films on the surface of the substrates. Temperature was measured by iron-constantan thermocouples positioned at the center of the underside of the slides. The temperature was controlled by a variable transformer which regulated the current through the heaters.

Two beam fluxes were tested. A high flux was obtained by heating the molybdenum boat to a white-yellow heat for about 5 to 10 seconds, during which time most of the zinc in the boat (usually around 0.5 g) was vaporized. A low flux was obtained by heating the molybdenum boat to a low, dull-red glow which was barely visible. The zinc was heated in this manner for 1 to 5 minutes, and about 0.2 g of zinc was vaporized.

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*This glass is treated by etching and heating to form a synthetic quartz.

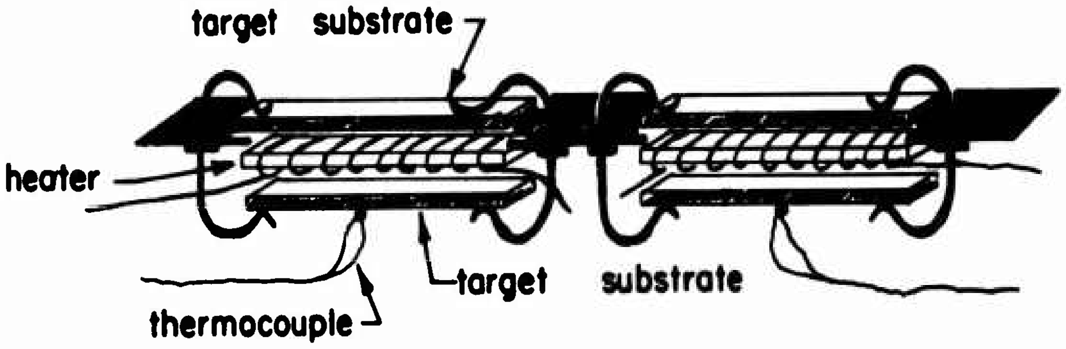

Figure 2.2 Target assembly.

2.2 Experimental Methods.

Because an exact measurement of the sticking coefficient of zinc on glass was difficult, if not impossible, with the apparatus available, it was decided to use an approximate visual method to estimate the ratios of sticking coefficients without actually evaluating their absolute values. This visual analysis depends on the wide difference between the sticking coefficient for zinc-on-zinc [reported by Wessel (Reference 7) to be unity], and the sticking coefficient for zinc-on-glass [reported to be much less than unity by Fray and Nielson (Reference 8)]. On the basis of the observations of Yang, et al. (Reference 11), and Devienne (Reference 5), that sticking coefficients increase as the thicknesses of the deposit increase, and because of the great difference between the sticking coefficient for zinc-on-glass and zinc-on-zinc, a plot of the film thickness versus time of bombardment can be expected to take the general form shown in Figure 2.3. When the film thickness reaches point L_a (probably between 1 and 5 atomic layers), a transition occurs from zinc-glass sticking to zinc-zinc sticking, and the rate of growth increases sharply to produce the curve shown. When the curve reaches the point L_b, its presence is visible (probably at 20 to 50 atomic layers). Relative to the length of time it takes for formation of the first five monolayers, the additional time necessary for build-up to

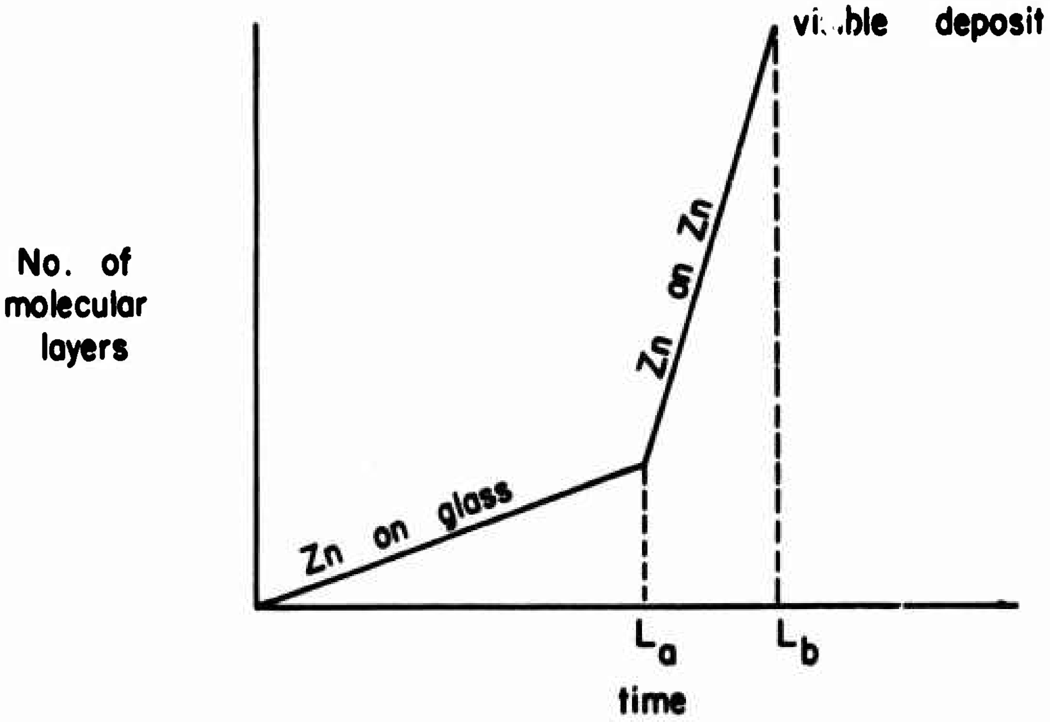

Figure 2.3 Film thickness as a function of time.

a visible deposit might be considered almost insignificant (i.e., the distance between L_a to L_b is very small when compared with the distance from 0 to L_a). Thus, the length of time to form a visible deposit is used as an approximate indication of the sticking coefficient. A mathematical presentation of this approximation has been discussed by Houseman (Reference 30).

A series of six experiments were conducted according to the following procedures. Results are presented in Section 3.

Experiment 1.

Comparison of the nucleation rates of zinc on three different types of glass was made with ordinary microscope slides, Vycor, and Corning substrate glass. Each type of glass was cleaned in nitric acid as previously described and placed into a metal slide holder above the zinc beam source in the vacuum chamber. Each run involved a pair of glass slides of each type of glass: all slides were preheated to 65° C and then allowed to cool to their respective experimental temperatures. One of each type was held at 27° C, or room temperature, and the other was held at 55° C. Deposition of zinc onto the substrate was carried out at a high flux, the molybdenum boat being heated for 5 seconds to a white heat.

Experiment 2.

The effect of the cleaning procedure on the sticking of zinc on glass was studied with two sets of ordinary microscope slides. One was cleaned in a dichromate cleaning solution, the other in nitric acid. Both slides were outgassed in a vacuum of 10^{-6} torr by heating them to 70° C for 2 hours. They were then allowed to cool to a temperature of 55° C and maintained at this temperature throughout the experiment. Deposition of zinc was carried out at a high flux.

Experiment 3.

The influence of substrate temperature on the sticking of zinc was studied with one slide sample at room temperature and the other at 65° C. Both slides were initially cleaned with nitric acid and were outgassed in vacuum by heating them to 70° C for 4 hours. The slides were then allowed to cool, one to room temperature and the other to 65° C. A high flux of zinc atoms was employed.

Experiment 4.

The effect of flux on nucleation rate was examined. The procedure of Experiment 3 was repeated at considerably lower flux. The molybdenum boat containing the zinc was heated to a barely visible red glow. This heat was maintained for about 10 minutes.

Experiment 5.

Five slides were installed in the vacuum chamber, and a five-slide heater was used to give a temperature gradient from slide to slide as illustrated in Figure 2.4. The heaters consisted of nichrome wire wound about the middle 3/4-inch section of each microscope slide; the number of windings around each slide was varied so that each slide was at a different temperature. These resistance heaters were connected in series and each heater was sandwiched between a pair of glass slides which served as target substrates. The glass slides were outgassed in vacuum for 5 hours by heating the coils, giving a gradient heating of approximately 95, 75, 55, 45, and 25° C. These temperatures were maintained during the vaporization of the zinc which was performed at a low flux. The temperature of the slides was monitored by thermocouples held to the center of the first and fourth slides.

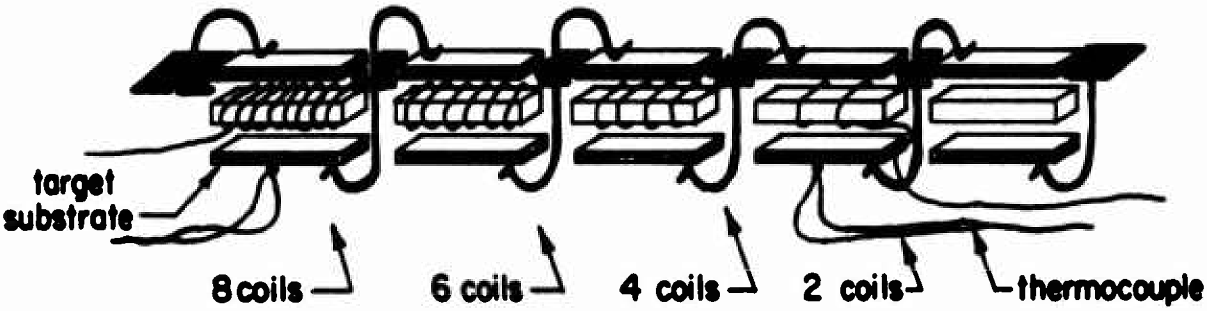

Figure 2.4 Experimental setup to study effect of substrate temperature.

Experiment 6.

A programmed experiment was conducted to show the definite influence of substrate temperature on the adsorption of zinc on glass. A glass slide was first cleaned by nitric acid and outgassed in vacuum for four hours at a temperature of 80° C. It was then allowed to cool to room temperature and exposed for 4 minutes to a low flux of zinc atoms. The glass slide, showing no evidence of zinc nucleation, was then slowly heated to 75° C during which time there was no vaporization of zinc. Any zinc vapor striking the glass surface during the substrate heating process was left from the prior zinc vaporization. During this portion of the experiment the pressure was 10^{-6} torr.

3. RESULTS

The results of experiments 1 through 6 are:

Experiment 1.

There was no difference in the deposition rate of zinc on acid-cleaned substrate glass, Vycor, or lime glass. Zinc deposits appeared simultaneously on all three types of glass slides heated to 65° C about 15 seconds after the zinc vaporization was initiated. No deposition was observed on any of the glass samples held at room temperature even after 10 minutes of exposure to the zinc vapor.

Experiment 2.

Cleaning the glass surface with nitric acid or with dichromate cleaning solution did not affect the deposition rate, but it did influence the appearance of the condensed film. The slides cleaned with dichromate cleaning solution and those cleaned with nitric acid showed almost immediate zinc adsorption. However, the zinc film on the dichromate-cleaned slide was slightly irregular in nature, whereas the zinc deposit on the nitric acid-cleaned slide was continuous and uniform in nature.

Experiment 3.

Substrate temperature had a definite effect on the sticking coefficient for zinc. Zinc adsorption was observed to occur almost immediately on the slides held at 60 to 65° C after vaporization of the zinc was initiated. The slide held at room temperature showed no sign of zinc deposition even after being exposed to a high flux for 15 minutes. These observations have been confirmed in three separate trials.

Experiment 4.

As in the previous experiment, there was no sign of deposition of zinc on the slide held at room temperature. Also, no immediate zinc film was observed on the glass slide heated to 50° C in contrast to the deposition behavior at high flux. Instead, only a small "smudge" of zinc appeared on the slide after approximately 4 minutes of very slow zinc vaporization. The zinc film was not the continuous film that had been observed in previous experiments, but some preferential sticking to certain areas of the glass slide was noticed. This was attributed to differences in the surface composition of the glass* rather than to improper cleaning since this same preferential sticking appeared in repeated experiments.

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*Small "islands" of zinc deposit appeared in a definite pattern on the glass slide which is believed to conform to the stresses on the glass as a result of being pulled from the molten glass state.

Experiment 5.

The formation of a visible film of zinc on the 95° C slide was observed within 10 seconds of initiation of zinc vaporization. After approximately 3 minutes of exposure to the zinc vapor, a zinc smudge appeared over the region of the heating coils on the slide at approximately 75° C. During this time there was also a slow extension or growth of the original zinc smudge on the 95° C slide toward the cooler periphery of the slide. After about 5 minutes of exposure to the low flux there appeared a slight streaking of zinc on the slide heated to approximately 55° C. Even after 10 minutes, however, no sign of a deposit appeared on either the 45° C or the 25° C slides.

In addition, it was noted that the pattern of the zinc deposit varied with the substrate temperature. The small temperature gradient formed on each of the slides, due to the positioning of the heating coils in the center of the slides, showed different coloration of zinc deposits with different temperatures. The zinc deposited directly over the coils of the 95° C slide was a shiny, silvery film. The deposit of zinc on the same slide, slightly removed from the coils, was powdery and silvery-white in appearance.

Experiment 6.

There was no deposit noted on the slide during the low flux vaporization of zinc. After the zinc had been completely vaporized and the temperature of the slide gradually raised to 75° C, there was evidence of zinc sticking although the film was not as opaque as in previous experiments. It was noted that the zinc deposit appeared 3 minutes after completion of the zinc vaporization when the pressure reading was below 10^{-6} torr.

4. DISCUSSION

An important factor in nucleation kinetics is the composition of the adsorbed layer on the substrate surface. Wexler (Reference 1) refers to this and points out that the variation of sticking coefficients within a defined system is due to the difficulties of surface reproducibility. Earlier work at Goucher College (Reference 31) has shown that slides cleaned with HCl gave uniform and continuous adsorption of zinc at 65° C whereas the same type of glass cleaned with strong base, KOH, showed blotchy and irregular adsorption patterns (Reference 32). From the experiments described in this paper, it has again been noted that continuous and uniform zinc deposits appeared on acid-cleaned glass. For both the nitric acid-cleaned and the dichromate-cleaned surfaces, the deposition rates for zinc were the same.

This phenomenon might be explained in terms of the chemistry of glass. McMarlin (Reference 33) has described the structure of glass as shown in Figure 4.1. According to the model, the surface is chemically uniform with hydrogen atoms in the most exposed positions. Various surface adsorbents become associated with the glass surface; yet, if a fresh-glass surface is treated with water, most of the adsorbed film will consist of water molecules. Since the glass surface acts as a weak acid, treatment of its surface with a strong base will probably result in replacement of the surface hydrogen with another cation. In addition, the entire base molecule might be adsorbed, just as the water molecules were, to the surface of the glass. These molecules adsorbed on the surface according to Hirth and Pound (Reference 34), Chirigos, et al. (Reference 13), and Devienne (Reference 5) would be expected to act as contaminants and to lower the sticking coefficient. Treatment of the glass by water rinsing or by heating the glass would probably not remove all of this adsorped contamination. It has also been reported (Reference 35) that SiO_2 is preferentially dissolved by KOH washing and the surface is left richer in metallic oxides. Thus, base-cleaned glass would be expected to show areas with low sticking coefficients and this would explain the blotchy zinc adsorption that was observed. Treating the surface of glass with an acid would remove contaminating surface films and would also give the surface a chemically uniform nature. The water adsorbed during the water rinses could be removed during the outgassing of the slides. Thus, any reaction involving the surface would be uniform and, if adsorption takes place, the film would be continuous.

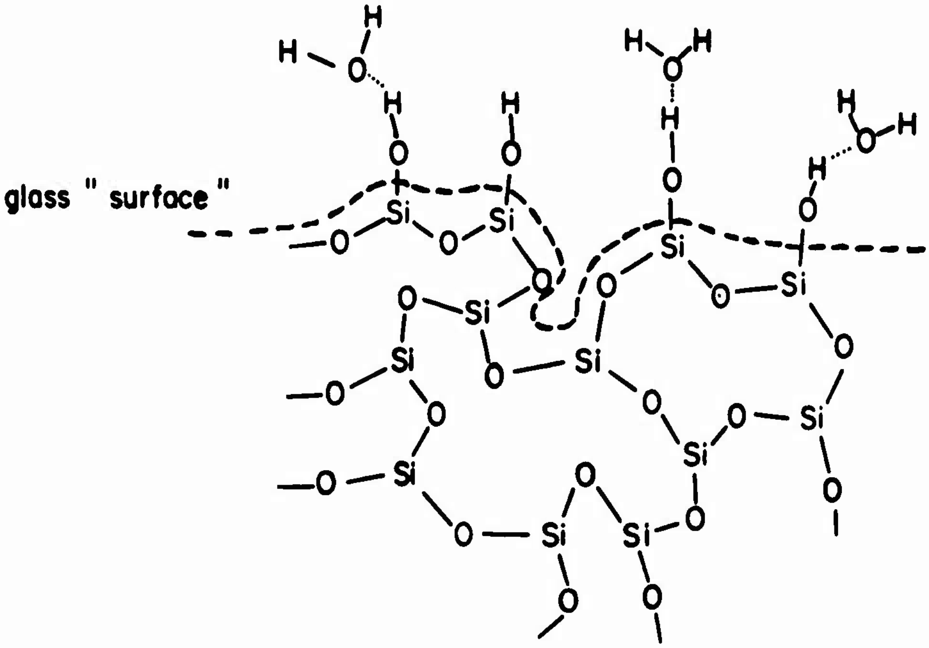

Figure 4.1 Two-dimensional structure of glass.

The influence of substrate temperature on the sticking coefficient of zinc can be explained in several ways. Using the approach of a number of investigators including Wexler (Reference 1), Devienne (Reference 2), and Cockcroft (Reference 23), the influence of temperature might be attributed to surface composition change. The removal of water and other adsorbed contaminants from the substrate surfaces at temperatures above 50° C could cause the observed increase in the sticking coefficient at these temperatures. The conditions of these experiments, which include extensive periods of outgassing at 95 to 100° C for both hot and cool surfaces, and at least three flushes of the system with helium, would seem to minimize the likelihood of differences in composition of the adsorbed layers on the hot and cold surfaces. (It is estimated that repeated flushing with helium reduced the oxygen partial pressure to less than 10^{-12} torr; under these circumstances, coverage of the surface by oxygen adsorption would require more than 9 hours per monolayer).

It is also possible that the observed increase of sticking coefficient with temperature is the result of a condensation mechanism in which the zinc atoms are retained by the glass surface because of the formation of a stable zinc-oxygen bond. An increase in temperature could enhance the kinetics of this process either by increasing the case of zinc-oxygen bonding or by weakening the hydrogen-oxygen bonds in the surface layer and increasing the probability of replacement of a hydrogen atom by a zinc atom.

A third possibility is that surface mobility plays an important role in the condensation process for zinc and that this is enhanced in this temperature range more by a temperature increase than by the factors which increase the tendency to reevaporate.

Holloman and Turnbull (References 36 and 37), in their work on heterogeneous nucleation, have proposed a mechanism of film deposition in which an impinging molecule resides on a surface, essentially immobile, for a finite length of time and then reevaporates. However, during the residence period if more impinging molecules are able to create a critical nucleus at that location, a crystal would grow as more impinging molecules strike favorable lattice sites and are retained.

Pound, Simnad, and Yang (Reference 38), and before them, Frenkel (Reference 28), have proposed a condensation mechanism in which impinging atoms move at random along the surface much like a two-dimensional gas until they evaporate or join another atom or cluster of atoms. These clusters grow by more collisions of molecules in the adsorbed layer (and shrink by evaporation) until the critical nucleus is attained.

Wexler (Reference 1), in comparing these two mechanisms, has pointed out that it has been impossible to distinguish between them because the rate equations produced by both are similar. It seems possible that most deposition mechanisms lie somewhere between these two extremes of no mobility and unhindered mobility and that condensing molecules possess varying amounts of mobility during their stay on the surface; the amount of mobility depends on the strength of the binding energy between the adsorbate and the surface. One would expect extensive surface diffusion in cases where the binding energies between condensate and substrate are low (under which circumstances the mean residence time would be short) and very little, if any, surface diffusion where the binding energies between condensate and substrate are high. Since high binding energies are predictive of high sticking coefficients (References 1 and 39), one might expect substances with high sticking coefficients to show direct lattice addition.

Thus, the temperature dependence of the sticking coefficient of a particular vapor-substrate combination can be expected to depend upon the relative importance and temperature dependence of retention time and surface mobility in the crystal forming process. Two general types of situations could exist:

1. Vapor-glass binding energy and sticking coefficient are high. Surface mobility would be unimportant, the mechanism of direct addition prevails, and a temperature increase would decrease retention times and the sticking coefficient as well. If, however, the average retention time is long with respect to the time between collisions, one would expect the temperature effect to be very slight or even negligible.

2. Vapor-glass binding energy is low, and the condensation coefficient (which is low) depends on both retention time (which decreases with a temperature increase) and surface mobility (which increases with a temperature increase). Three possible cases arise:

   a. If the effect of decreased retention time predominates, one would predict a negative slope for a graph of sticking coefficient versus temperature.

   b. If the effect of increased mobility predominates, one would expect an increased sticking coefficient with increased temperature.

   c. If neither of these temperature effects is dominant, the effects will tend to cancel each other and produce only weak temperature dependence for the sticking coefficient.

The rule of thumb for plating zinc on glass is that a drop in temperature of the substrate from +25° C to -25° C does not particularly improve the poor sticking of zinc, but zinc does stick almost completely at liquid nitrogen temperatures. That is, the sticking coefficient of zinc on glass is strongly temperature dependent in the temperature region between -200° C and -25° C (case 2a), but is only weakly temperature dependent in the temperature region around 0° C (case 2c). The data reported here indicate that zinc exhibits the behavior described in case 2b in its condensation on glass between 25° C and 100° C.

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13. ABSTRACT

The influence of glass substrate temperature between room temperature and 95° C on the sticking coefficient of zinc-on-glass in a vacuum of 10^{-6} torr was studied. The sticking coefficient was found to be significantly higher at 65 to 95° C. At room temperature no adsorption of zinc was observed even after the glass surface was exposed to a high flux of zinc vapor atoms for 15 minutes.

Contamination effects on the sticking coefficient are described; it was noted that at temperatures within the range of 65 to 95° C a uniform and continuous film of zinc deposited on glass slides cleaned with nitric acid and water. The effect of change in the flux of the zinc vapor on the sticking coefficient is also discussed. Three theories are proposed to explain the phenomena of increased sticking of zinc with increased substrate temperature.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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Zinc adsorption						
Contamination effects						
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