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Nucleation and growth of condensate clusters on solid surfaces

YUH LANG LEE, JER RU MAA
Department of Chemical Engineering, National Cheng Kung University, Tainan, 70101 Taiwan

The nucleation and growth of the condensate clusters during the early stages of the vapour deposition process were studied by depositing silver vapour on silicon, glass, mica, NaCl and KBr in a small coater. It was observed that the formation of the condensate film can be divided into four stages and the condensate clusters exhibit liquid-like behaviour during their early stage of growth. The mode of cluster growth is affected by the interfacial properties between the condensate and the substrate. The effect of surface roughness on the cluster growth is relatively insignificant and the experimental reproducibility is usually poor because of unavoidable contamination.

1. Introduction

The nucleation and growth mechanism of the condensate clusters during the early stages of the vapour deposition processes have been known to have a strong influence on the thin film properties. It is believed that the vapour molecules are first adsorbed on the substrate surface [1]. The adatom may re-evaporate before being captured by other adatoms or clusters. The mean resident time of the adatom on the substrate is determined by the Frenkel equation

$$\tau = 1/\nu \exp(E_a/kt) \qquad (1)$$

where E_a and ν are the energy of adsorption and the vibration frequency of the adatom, respectively. During the period that they stay on the substrate, the adatoms may migrate two-dimensionally. The surface diffusion coefficient is

$$D = D_o \exp(-E_d/kt) \qquad (2)$$

where E_d is the activation energy of surface diffusion, $D_o = a_o^2 \nu$, and a_o the distance an atom covers in one jump. The diffusion and collision of the adatoms lead to the formation of the critical nuclei. Once a condensate cluster reaches the critical size, it becomes stable and will keep on growing. Since solid surfaces can hardly be made perfectly smooth and homogeneous, the critical nuclei are usually formed at various favourable sites [2–6]. The process of heterogeneous nucleation is further complicated by unavoidable contamination and, therefore, its experimental reproducibility is usually very poor.

The condensate clusters on solid substrates grow by capturing the adatoms and by direct vapour impingement. The first path is more important when the cluster is small in comparison with the mean surface diffusion distance $(D\tau)^{1/2}$. The importance of the vapour addition increases as the clusters grow larger [7, 8]. The condensate clusters also grow by coalescence which includes mobility coalescence and growth coalescence [9–12]. The mobility coalescence is more important when the clusters are small and their mobility is high. As the clusters grow larger, growth coalescence becomes the dominating route of growth.

2. Experimental procedure

In this work, silver films were deposited on various substrates in a small coater of model ULVAC VPC-260 made by the Sinku-Kiko Co. The vacuum in a glass bell jar of 300 mm I.D. and 300 mm high was maintained by a rotary mechanical pump and a diffusion pump. A Knudsen cell, with a 3 mm diameter orifice, was used as the source of the silver vapour. The evaporation rate was controlled by the cell temperature which was measured by a ceramic-sealed thermocouple fitted to the inside of the cell.

The materials chosen as substrates were silicon, glass, mica, NaCl and KBr. Fresh cleaved surfaces were used for the cases of NaCl, KBr and mica. The procedure for the cleaning of silicon wafer was as follows.

(1) Ultrasonic treatment in trichloro-ethylene
(2) Supersonic treatment in acetone
(3) Immersion in H_2SO_4–H_2O_2 (3:1) solution for 6 min.
(4) Immersion in concentrated HNO_3 for 6 min
(5) Etching with H_2O–HF (10:1) solution for 20 s
(6) Washing with distilled water and then drying.

Glass substrates were cleaned by ultrasonic treatment in a detergent solution, trichloroethylene and acetone, washed with distilled water and dried. Silicon wafers were also polished by Al_2O_3 powder of 5, 0.5 and 0.05 μm in order to give substrates of different surface roughnesses. After the pre-treatment steps, the substrates were placed in the substrate holder. The substrates were positioned along a circle of 60 mm in diameter coaxial with respect to the orifice of the Knudsen cell in order to obtain the same rate of vapour impingement so that a number of different substrates could be coated at the same time under the same conditions. The distance between the vapour source and the substrates was 130 mm and the deposition time was controlled by a moveable shutter. When a series of films with a different deposition time was desired, the substrates were placed on a moveable holder and the vapour source was enclosed in a metal box with a hole right above it. The distance between this hole and the vapour source was 120 mm. By adjusting and moving the holder correctly one is able to obtain a sequence of specimens of various deposition time in one run. A substrate was kept as close as possible to the hole during its turn of deposition so that the vapour beam can impinge only on this particular substrate.

After the system was evacuated to 10^{-5} torr the substrates on the holder were heated at 300 °C for 30 min, in order to get rid of any contamination, and the temperatures of the substrate and the evaporator were adjusted to the desired values before the deposition process began. Right after the silver deposition, without breaking the vacuum, a carbon film was also deposited in order to 'fix' the silver film. For the purpose of visualization with the transmission electron microscope (TEM), the substrates were detached from the film by dissolving in water (NaCl, KBr) or HF solution (Si, glass, mica) and the silver film accompanied by the carbon film was left for observation supported by a copper grid.

3. Results and discussion

3.1. Stages of growth

A sequence of pictures of different stages of film growth was obtained by varying the time of deposition, as shown in Fig. 1. The substrate material was glass and the temperatures of the vapour source and the substrate were 1000 and 25 °C, respectively. The four stages of the growth process of the deposited film pointed out by Pashley *et al.* [13], island stage, coalescence stage, channel stage and continuous film, can also be observed in this figure. The cluster density increases gradually to a maximum and then decreases due to the coalescence of the clusters. The cluster size also increases during the deposition process. This is verified by the electron diffraction patterns shown in the same figure.

3.2. Liquid-like behaviour of clusters

Except for a few cluster pairs which exhibit the neck of connection, almost all clusters shown in Fig. 1 are round in shape. This does not mean that no coalescence happens to these clusters but that a rapid reforming mechanism takes place during the contact of clusters. This rapid morphological change with the liquid-like behaviour was first observed by Bassett [14] and explained in terms of sintering theory by Pashley *et al.* [13]. The driving force of the liquid-like behaviour is the minimization of surface energy by reduction of the surface area and the formation of preferred planes. The mass transport mechanisms involved in coalescence are evaporation, condensation, volume diffusion and surface diffusion. Evaporation and condensation are mass transfer processes which take place at various parts of a coalescence pair due to the difference in vapour pressure which results from the difference in surface curvature. At the beginning of coalescence, when two clusters just come into contact, their shape could be considered as that shown in Fig. 2

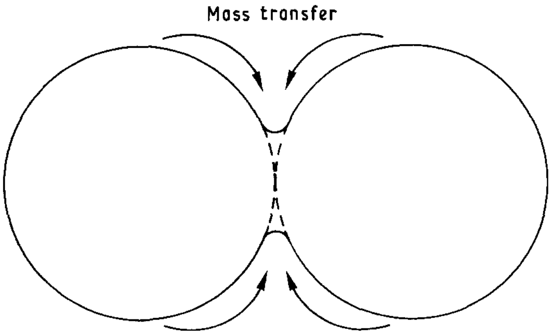

Figure 2 Evaporation and condensation mechanisms for two clusters come into contact.

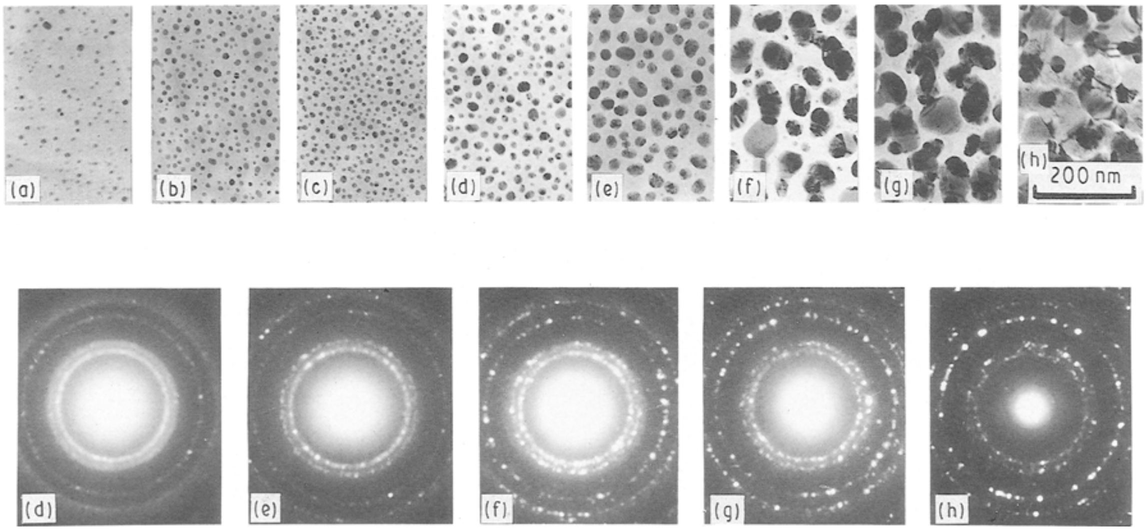

Figure 1 Film growth of the Ag–glass system under various deposition time (a) 5 s, (b) 10 s, (c) 15 s, (d) 30 s, (e) 60 s, (f) 90 s, (g) 120 s, (h) 180 s (evaporation temperature 1000 °C, substrate temperature 25 °C).

[15]. At the outer surface of the cluster, there is a positive radius of curvature, so that the vapour pressure is larger than that for a flat plane. At the surface of the neck of connection, there is a negative radius of curvature and a vapour pressure one order of magnitude lower than that for the cluster itself. This vapour pressure difference causes the mass transfer from the outer surface of the cluster to the neck area. Under the impingement of vapour atoms this vapour pressure difference between the neck area and the outer surface of the cluster pair causes the neck area to have larger driving force for the atoms to add. In other words, the neck is a better 'sink' of atoms, and the captured atoms could stay more stably at the neck. Besides, there is much evidence to suggest that the surface diffusion is the predominant route of cluster growth especially for the smaller ones [23].

3.3. Effect of substrate material

For the purpose of studying the dependence of the cluster formation and growth on the interfacial parameters, five materials were chosen as substrates: silicon wafer polished with Al_2O_3 powder of 0.05 μm, glass, mica, NaCl and KBr. The temperatures of the vapour source and the substrate were kept at 900 and 25 °C, respectively. Figs 3 and 4 show the distributions of Ag clusters on these substrates with deposition times of 90 and 120 s, respectively. The cluster density is much larger and the cluster size is smaller for silicon than that for the other substrates. This implies that the silver–silicon system has higher E_a and E_d (large τ and small D) than the other systems and is in agreement with the difference in the modes of crystal growth [16–18]. The growth of Ag clusters on Si (1 1 1) belongs to the Stranski–Krastanov mode (layer plus island growth mode), while the other systems belong to the island growth mode that is, the adhesion force between silver and silicon is larger than that for the other systems and so to the value of E_a and E_d. It is hence not difficult for us to realize why the Ag–Si (1 1 1) system has a higher rate of cluster formation and smaller cluster size.

Both the Ag–NaCl and the Ag–KBr systems are of the island growth mode but the Ag–NaCl system has a higher cluster density and smaller cluster size than that of the Ag–KBr system as shown in Figs 3 and 4. This is in agreement with the values of the interfacial parameters obtained by Stowell [19], Donohole and Robins [20] and Venables [21] as listed in Table I.

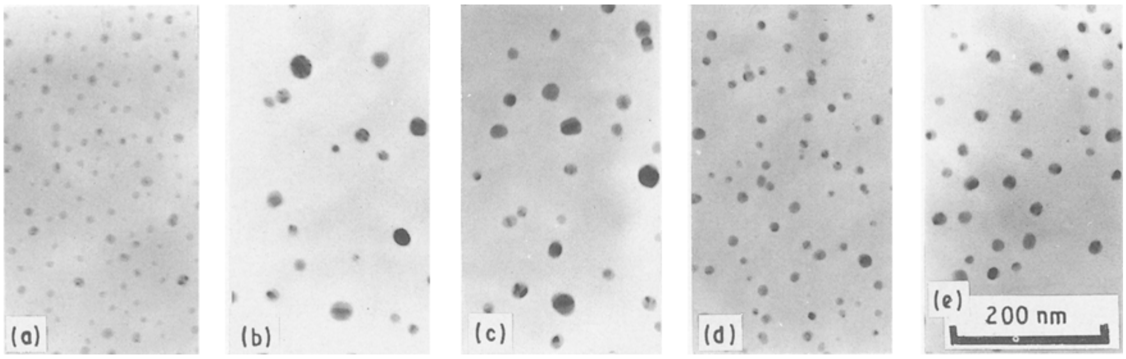

Figure 3 Ag film growth on various substrates: (a) Si (1 1 1), (b) glass, (c) mica, (d) NaCl, (e) KBr. (evaporation temperature 900 °C, substrate temperature 25 °C, deposition time 90 s).

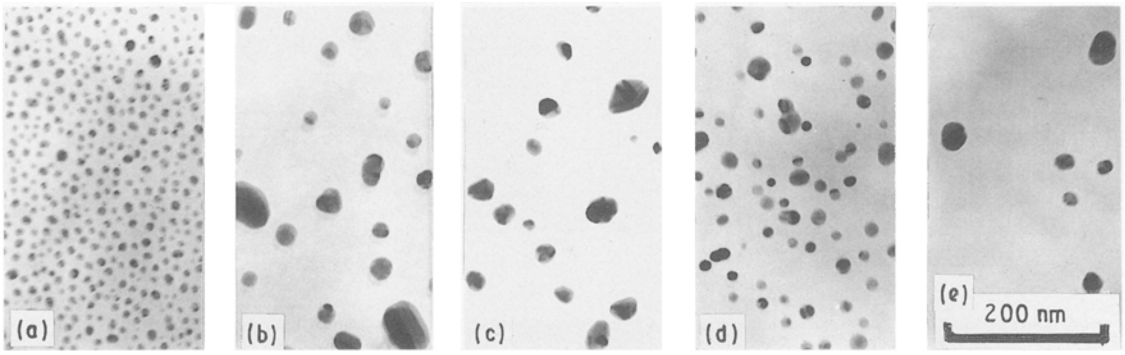

Figure 4 Ag film growth on various substrates (a) Si (1 1 1), (b) glass, (c) mica, (d) NaCl, (e) KBr. (evaporation temperature 900 °C, substrate temperature 25 °C, deposition time 120 s).

TABLE I

	E_a (eV)	D_o [19]	E_d (eV) [19]
Ag–NaCl (1 0 0)	0.61 [19], 0.63 [20], 0.65 [21]	5.8×10^{-6}	0.19
Ag–KBr (1 0 0)	0.47 [19], 0.46 [20], 0.52 [21]	2.1×10^{-5}	0.19

The Ag–NaCl system has larger E_a and smaller D_0 than that of the Ag–KBr system. From the cluster sizes and densities of the Ag–glass and Ag–mica system shown in Figs 3 and 4, one can predict that they have similar values of E_a, E_d and D_0 and their adhesion forces are less than that of the other systems studied in this work.

3.4. Effect of surface roughness

For the study of the effect of surface roughness, silicon wafers polished by Al_2O_3 powder of 0.05 and 0.5 μ and unpolished silicon wafers were used as the substrates. The limited resolution of the scanning electron microscope (SEM), means that we were not able to distinguish the silicon wafer surface polished by Al_2O_3 powder of different particle sizes, as shown in Fig. 5a. The morphology of the unpolished surface of the silicon wafer is quite different from the polished ones, as shown in Fig. 5b. Deposition of silver vapour was carried out under various conditions. No obvious differences in cluster density and size distribution were, however, observed between the polished and unpolished wafer surfaces, as shown in Figs 6 and 7.

3.5. Effect of surface inhomogeneity

Under TEM, we often observed different regions of cluster growth even on the same specimen. This phenomenon is believed to be a result of the inhomogeneity of the substrate surface. As a consequence of this effect, all pictures shown in this paper are selected from the most frequently occurring regions under the same operating conditions. Fig. 8 shows the result of depositing silver vapour on unpolished silicon wafer with a deposition time of 10 s and vapour source and substrate temperatures controlled at 1500 and 25 °C, respectively. Fig. 9 shows the result of the Ag–glass

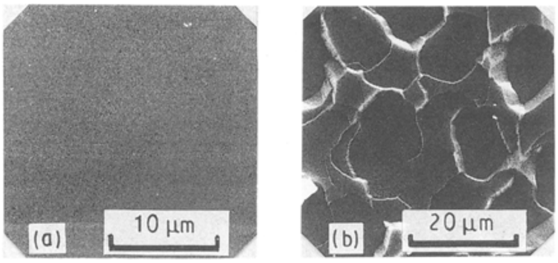

Figure 5 Surface morphology of silicon wafer (a) polished, (b) unpolished.

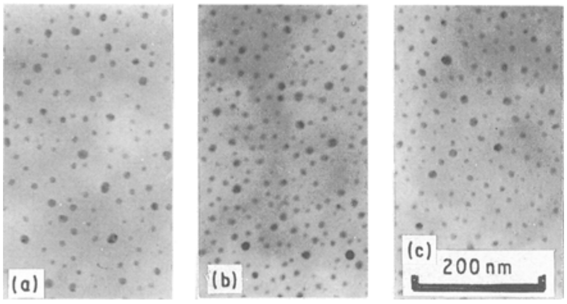

Figure 6 Ag film growth on silicon wafers polished by Al_2O_3 powder of various particle sizes. (a) 0.05 μm, (b) 0.5 μm, (c) unpolished. (evaporation temperature 900 °C, substrate temperature 25 °C, deposition time 90 s).

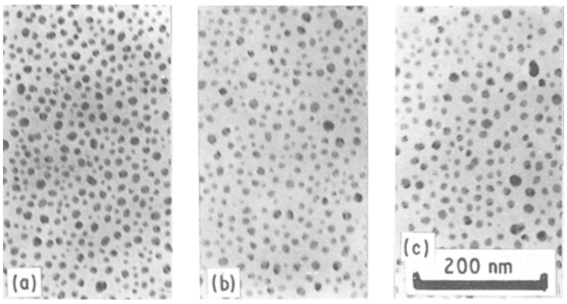

Figure 7 Ag film growth on silicon wafers polished by Al_2O_3 powder of various particle sizes. (a) 0.05 μm, (b) 0.5 μm, (c) unpolished. (evaporation temperature 900 °C, substrate temperature 25 °C, deposition time 120 s).

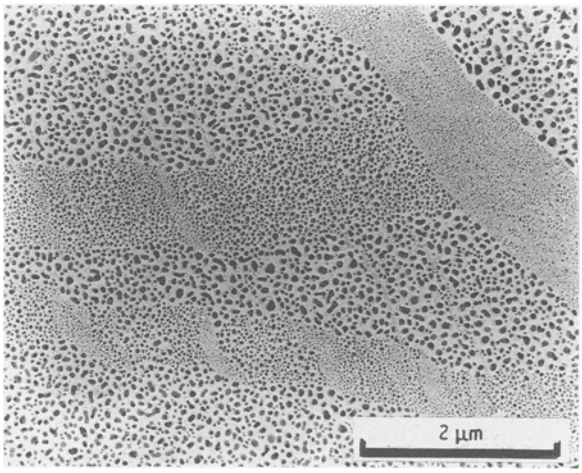

Figure 8 Effect of surface inhomogeneity to the film growth of Ag on unpolished silicon wafer. (evaporation temperature 1500 °C, substrate temperature 25 °C, deposition time 10 s).

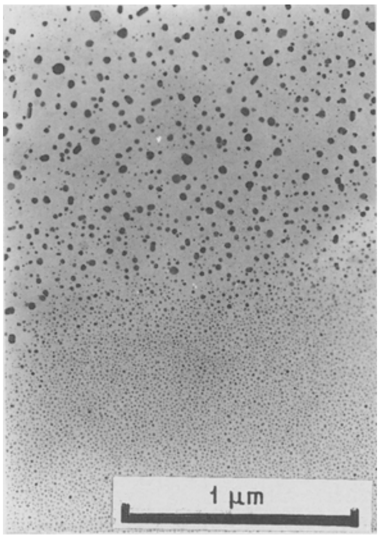

Figure 9 Effect of surface inhomogeneity to the film growth of Ag on glass surface. (evaporation temperature 900 °C, substrate temperature 25 °C, deposition time 45 s)

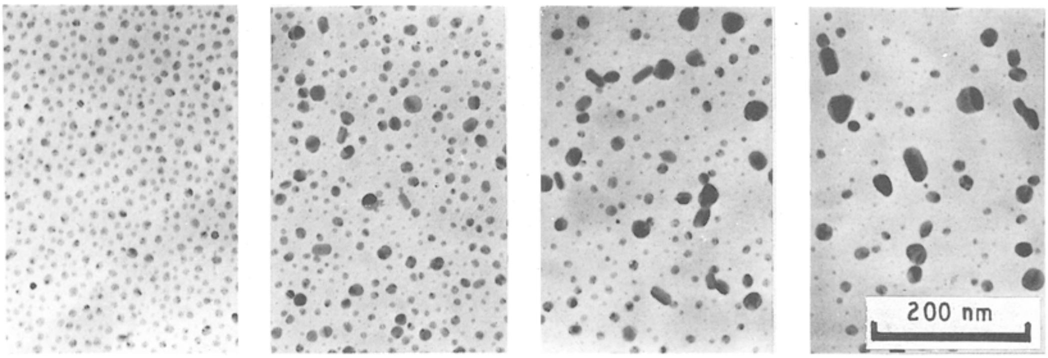

Figure 10 Cluster distribution of Ag deposited on glass surface. (evaporation temperature 900 °C, substrate temperature 25 °C, deposition time 30 s)

system with a deposition time of 45 s and vapour source and substrate temperatures controlled at 900 and 25 °C, respectively. Both of these two figures show distinct regions of relatively uniform distribution of cluster sizes and rather sharp boundaries. The regions of higher cluster density have a smaller cluster size and vice versa. This inhomogeneity of the substrate surface is perhaps caused by impurities. Impurity adsorption is likely to decrease the adhesion force of the deposit to the substrate and hence decrease the E_a and E_d values. This was verified by Rhead [22] who showed that the surface diffusion can be enhanced enormously by the presence of impurity adsorbates. In this work, a progressive variation of the cluster distribution, from a uniform-dense type to a dispersed-large grain type, as shown in Fig. 10, was also observed. This is likely to be caused by the concentration gradient of impurity adsorbed on the substrate surface.

4. Conclusions

In this work, silver vapour was deposited on silicon, glass, mica, NaCl and KBr. The effects of deposition time, substrate material, surface roughness and surface inhomogeneity on the cluster density and size distribution were studied by the post-deposition observation method.

In these systems, the mechanism of vapour deposition is composed of the adsorption of the vapour molecules on the substrate surface, surface diffusion, growth and coalescence of the deposit clusters. A sequence of stages of film formation: island, coalescence, channel and continuous film was also observed by using the electron microscope.

The driving force for the coalescence of clusters is resulted from the tendency of minimization of surface energy. The transport of mass occurs via the routes of evaporation–condensation and surface diffusion. The rapid reforming mechanism, means that all the clusters are round in shape.

The formation of the clusters is controlled by the interfacial parameters, E_a and E_d of the deposition system. Higher values of E_a and E_d lead to higher cluster density and smaller cluster size. It is often observed that on the same specimen, there are regions of lower cluster density and larger cluster size. This is perhaps caused by the adsorbed impurities which decrease the E_a value and increase the surface diffusivity, D, considerably. The difference in surface roughness causes no significant difference in the vapour deposition and the cluster formation.

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