YU ISSN 0015-3206
FZKAAA 18 (3) 253 (1986)

EARLY MECHANISM OF NUCLEATION AND GROWTH OF THIN EVAPORATED FILM OF GALLIUM

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Received 10 March 1986

Revised manuscript received 1 July 1986

UDC 538.95

Original scientific paper

The processes of nucleation and growth of a very thin film of gallium on carbon and NaCl substrates has been followed. A new technique is employed in preparing a very thin layer < 15 nm. The results of observation and the statistical analysis show that the film goes continuous on NaCl earlier through channel coalescence mechanism. On carbon the drop coalescence was predominant and the film still shows the isolated islands. In higher thickness, the primary, secondary and tertiary nucleations were observed.

1. Introduction

The effect of different parameters on the microstructure, orientation and mechanism of nucleation and growth has been followed by many workers. Most of this work was done on thicker overgrowth and for metals of high melting point. The early stages of nucleation and growth were followed kinetically by Eid$^{1,2)}$ for the very thin anodic films. The works of Pashley$^{3)}$, Murr and Inman$^{4)}$, Chopra$^{5)}$ and Behrndt$^{6)}$ have contributed valuable data for evaporated thin films. The mechanism of growth from thinner to thicker was the aim of this work. The effect of the substrate temperature has drawn much attention as well. The condensation of an overgrowth substrate proceeded by a step rule involving the formation of liquid nuclei or early clusters at high substrate temperature. This idea was suggested by Semenov$^{7)}$ and confirmed by Komnik$^{8)}$ for tin and indium.

The work of Pócza[9] and Singh and Murr[10] may be considered as the first trial for fabricating a nucleation and growth study in the early stages of nucleation and growth. The present work is dealing with the mechanism of nucleation and growth for a very thin film of gallium on carbon and NaCl substrates. The effect of the rate of evaporation on the mechanism of nucleation and growth was investigated. The analysis covered the range of thicknesses from ~1 nm up to 135 nm.

2. *Experimental techniques*

The gallium thin films were prepared by evaporation under vacuum of $\sim 10^{-4}$ Pa. Pure gallium of purity 99.999% was used. Different rates of evaporation were considered in the experiment. The temperature of the substrate was kept fixed at 291 K. The distance between the filament and the substrate was equal to 12 cm to avoid indirect heating of the substrates. The substrate employed in this work was a freshly cleaved (001) NaCl and an evaporated film of carbon. For thin films of gallium below 15 nm a backing layer of carbon was evaporated on it before stripping from the rocksalt. The thicknesses of the films of the order 15 nm and larger were measured by the interferometry techniques due to Tolansky[11]. The thicknesses below those and down to an average of 0.1 nm were deposited for a controlled time and rate. For that a camera shutter of speed as high as 1/250 s was employed. The substrates were shielded behind this shutter. An optical flat was suspended at the same geometrical coordinates of the substrates from the filament. Another mechanical shutter was used to shield the filament from the whole system. After the filament was heated to the suitable rate of evaporation, the mechanical shutter was released and the evaporation was completed for a suitable time to assure deposition of film thickness >100 nm on the optical flat. At the middle of this time the camera shutter was opened for any required pulse. The optical flat was then measured by interferometry and the rate of deposition was calculated. Accordingly the thickness of the film deposited on the substrate was estimated. In each run an optical flat was used to assure the thickness on the substrate.

3. *Results and discussion*

The condensation of a vapour atom is determined by its interaction with the impinged surface in the following manner.

The impinging atom is attracted to the surface by the instantaneous dipole and quadrupole moments of the surface atoms. As a result, the atom loses its velocity component normal to the surface in a short time, provided the incident kinetic energy is not too high. The vapour atom is then physically adsorbed, but it may or may not be completely thermally equilibrated. It may move over the surface by jumping from one potential well to the other because of thermal activation from the surface and/or its own kinetic energy parallel to the surface. The adatom has a finite stay or residence time on the surface during which it may interact with other adatoms to form a stable cluster and be chemically adsorbed (incorporated into the surface) with the release of the heat of condensation. If not adsorbed, the adatom reevaporates or desorbs into the vapour phase. Therefore, condensation is the net result of an equilibrium between the adsorption and desorption processes. The probability that an impinging atom will be incorporated into the substrate (surface) is called the condensation or sticking coefficient[12].

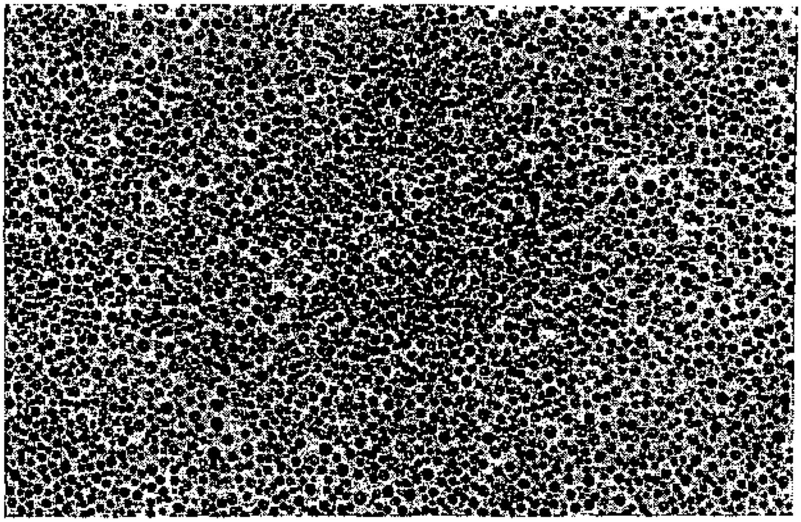

Fig. 1. Gallium film — × 3000 — 21.6 nm deposited onto amorphous carbon substrate with a rate of 1.8 nm s^{-1}.

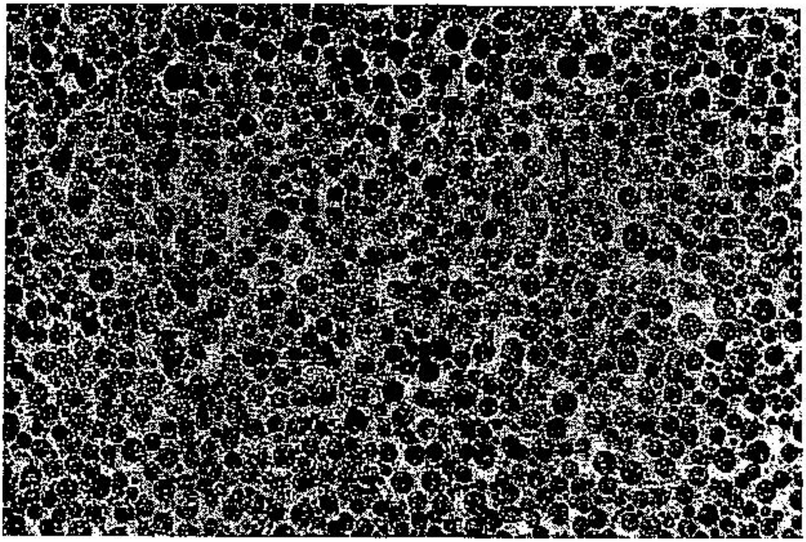

Fig. 2. Gallium film — × 3000 — 81 nm deposited onto amorphous carbon substrate with a rate of 1.8 nm s^{-1}.

Figs. 1—7 are examples of the transmission photographs recorded for the gallium thin films deposited on carbon and (001) of NaCl. It can be noticed that the film still retains the island behaviour even at the thicknesses larger than 100 nm. On the other hand, on crystalline substrates (001) NaCl the film go continuous as the thickness exceeds 66 nm. At smaller thicknesses the coalescence through

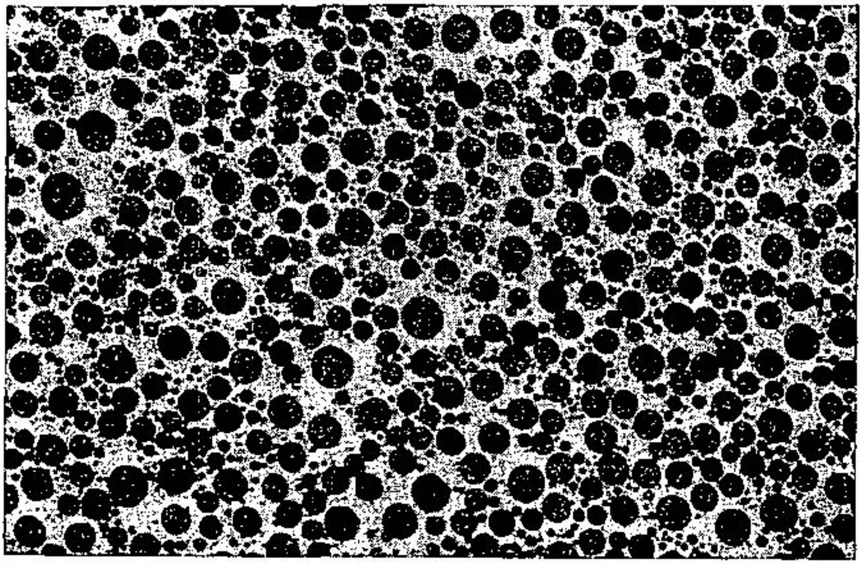

Fig. 3. Gallium film — × 3000 — 135 nm deposited onto amorphous carbon substrate with a rate of 1.8 nm s^{-1}.

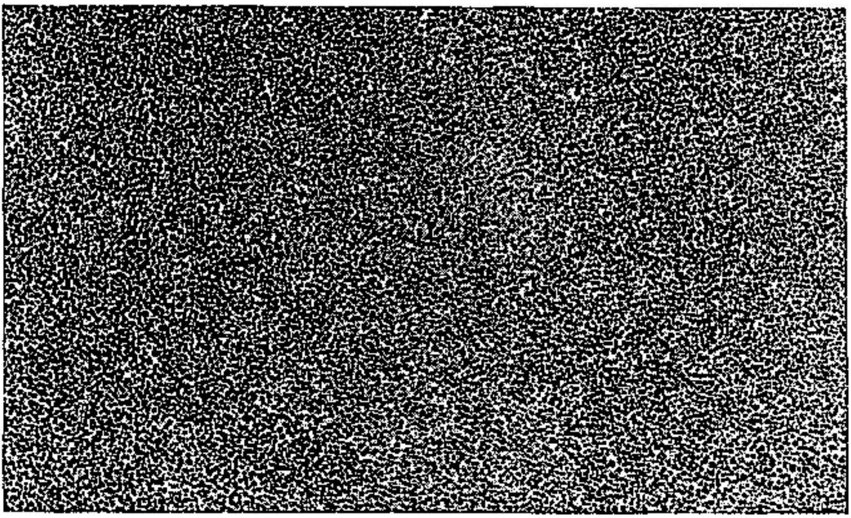

Fig. 4. Gallium film — × 3000 — 78 nm deposited onto amorphous carbon substrate with a rate of 4 nm s^{-1}.

channels are clear on NaCl as shown in Fig. 6. On the other hand this mechanism can not be identified on carbon, and the coalescence is direct between the spherical droplets. This could be a progressive mechanism due to surface diffusion of secondary nuclei to the primary ones as shown in Figs. 1—5. Statistical calculations

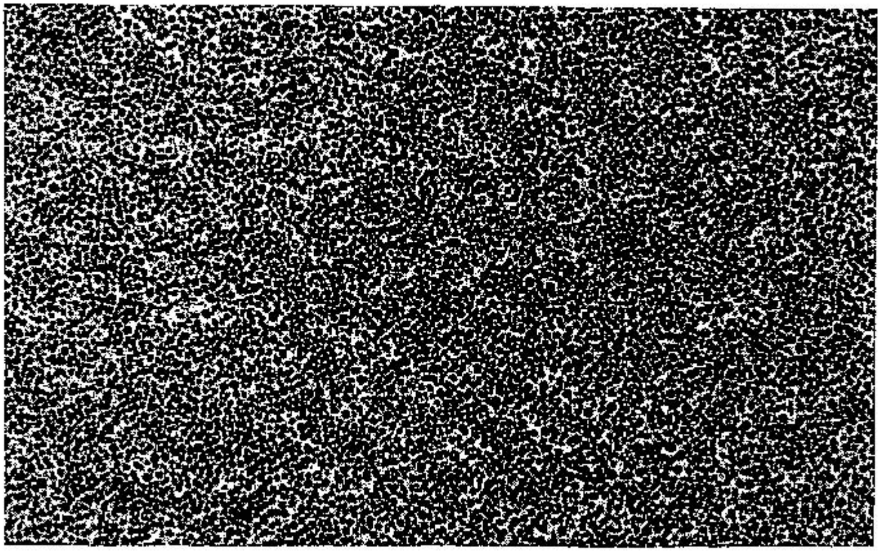

Fig. 5. Gallium film — × 3000 — 130 nm deposited onto amorphous carbon substrate with a rate of 4 nm s^{-1}.

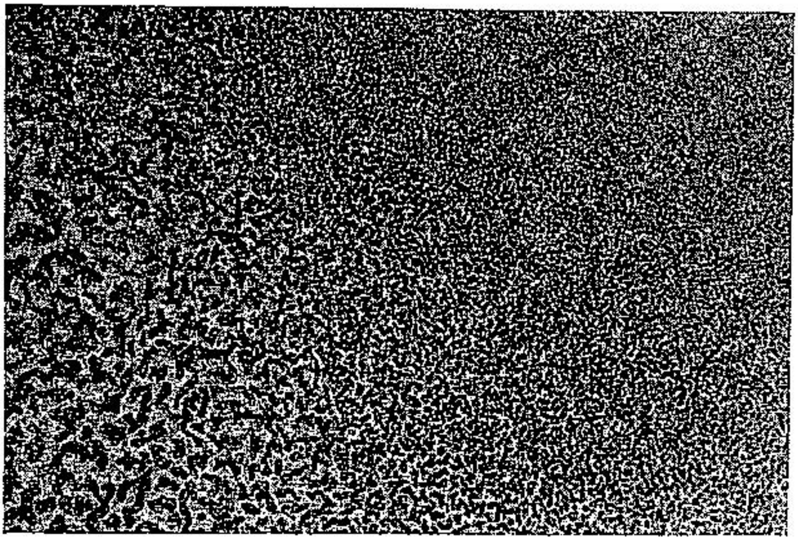

Fig. 6. Gallium film — × 3000 — 21.6 nm deposited onto cleaved (001) NaCl substrate with a rate of 1.8 nm s^{-1}.

were carried out for the average population and the island size as a function of thickness. The analysis was done for carbon substrates because the shape and the population can be easily identified. Fig. 8 shows the density of islands as a function of thickness. The least square deviation method was employed for fitting the experimental data. The tail of the curve is going down to very limited number of nuclei. This, of course, should be the stage of saturation which leads to the continuous layers. The figure shows that the density increases to a saturation value, then de-

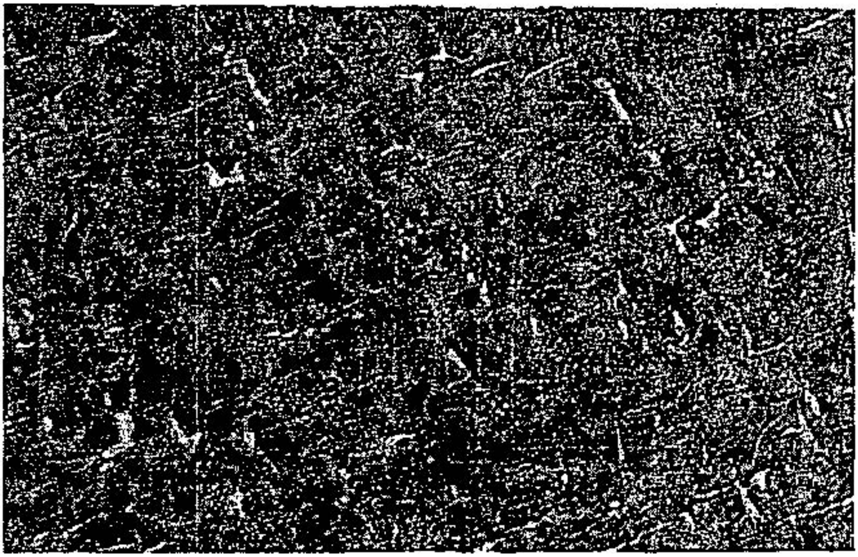

Fig. 7. Gallium film — × 3000—60 nm deposited onto cleaved (001) NaCl substrate with a rate of 1.8 nm s^{-1}.

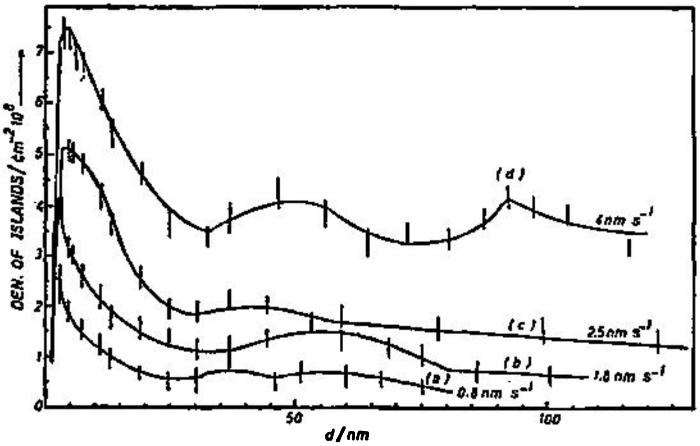

Fig. 8. Density of islands vs. thickness.
(a) 0.8 nm s^{-1}, (b) 1.8 nm s^{-1}, (c) 2.5 nm s^{-1}, (d) 4 nm s^{-1}.

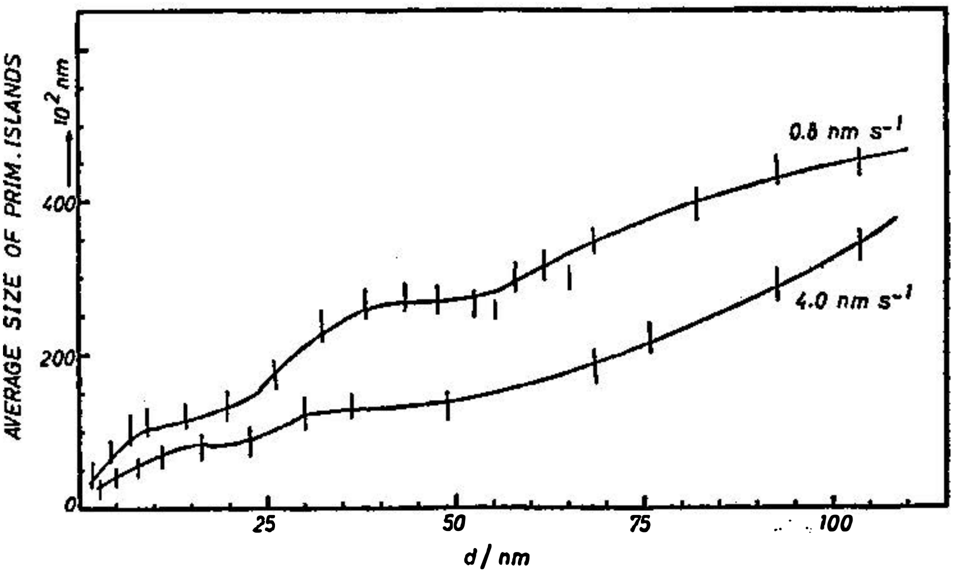

Fig. 9. Average size of primary islands vs. thickness.
(a) Rate of deposition 0.8 nm s^{-1},
(b) Rate of deposition 4 nm s^{-1}.

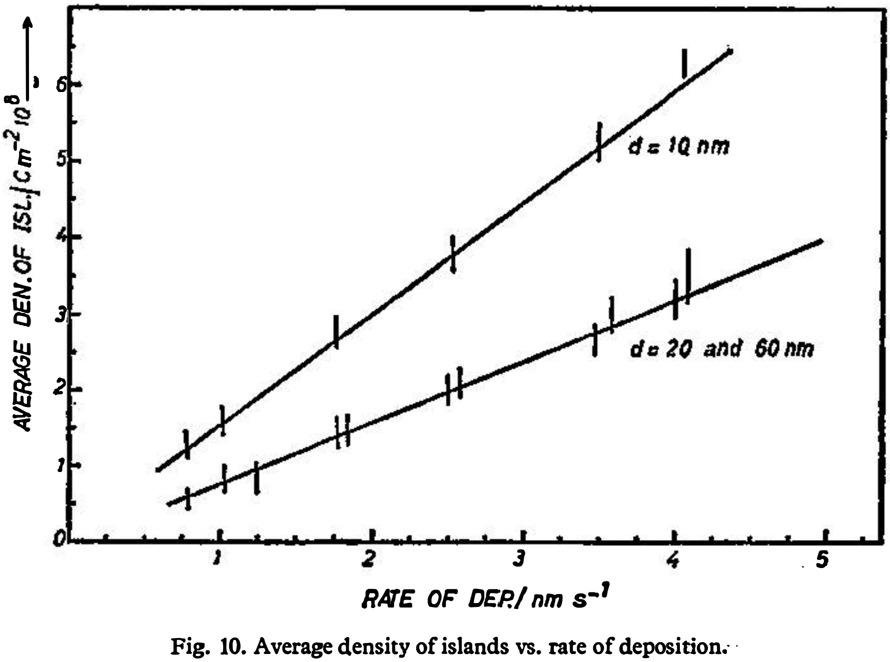

Fig. 10. Average density of islands vs. rate of deposition.
$d = 10$ nm, (b) $d = 20$ and 60 nm.

creases again with more broadened peaks. The general trend can be explained in terms of surface diffusion process and coalescence of the drops leaving bigger area for new secondary nucleation to take place. Fig. 9 shows the average size of the primary islands vs. thicknesses. From this figure the multi-plateau can be noticed. These plateau can be explained in terms of a progressive process of coalescence. As the size of the secondary island reaches a critical value, a coalescence step takes place. This process is different from the coalescence mechanism through channels, where the process is instantaneous i. e. the atoms from the vapour take place directly on the channels between the different islands till they become one island. This is repeated till the film go continuous as in the case of using NaCl in the present experiment.

The mechanism of coalescence for the present work is different from that suggested by the experimental work of Singh and Murr[10] for tin and indium. In their work they considered the coalescence between three-dimensional nuclei for which the rate of nucleation and growth are definitely different. In three-dimensional nuclei, most of the surface will be available for coalescence. On the other hand, in the present work, the two-dimensional nuclei are considered due to the spreading of the three dimensional nuclei on the surface. In this case the coalescence will be limited by the free edges of the nuclei. The surface diffusion will be very slow i. e. the nuclei will be dragged in a hopping motion different from that given for the three-dimensional nuclei. The droplet coalescence on NaCl was revealed. Fig. 10 shows the average density vs. the rate of deposition. It is clear from Figs. 4 and 5 and the linearity of this relation that the nucleation rate is predominant than growth. This idea was suggested in the early work of Eid[1,2]. A similar trend was found for the rate of nucleation and growth for the electro-deposited thin films. The same idea was suggested by Poppa[13] and Murr[14].

The derivation from linearity at higher rates may be explained in terms of the decrease of the area available for nucleation and the instantaneous process of coalescence which may take place between some of the energetic nuclei through undetectable surface diffusion.

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MEHANIZAM NUKLEACIJE I RASTA TANKIH EVAPORIRANIH FILMOVA GALIJA

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UDK 538.95

Originalni znanstveni rad

Primjenom nove tehnike priređivanja vrlo tankih filmova kojima je debljina manja od 15 nm ispitivani su procesi nukleacije i rasta tankih filmova galija na substratima ugljika i natrijeva klorida.