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DENDRITIC OXIDE GROWTH ON THE SURFACE OF LIQUID GALLIUM

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Abstract

We have studied the oxidation of a liquid gallium surface with a high spatial resolution scanning ion microprobe. A 40 keV focused gallium ion beam, extracted from a liquid metal ion source, was employed, first, to sputter clean a 40 x 40 μm^2 area on a drop of liquid gallium, in a ultra high vacuum (UHV) specimen chamber. It was then used to monitor the oxide growth by secondary ion mass spectrometry imaging microanalysis while the chamber was gradually back-filled with oxygen. In the initial stages, gallium oxide grew in a dendritic pattern from the edge of the cleaned area where oxide preexisted. Gradually the oxide layer grew in thickness and covered the entire area leaving only small islands and channels uncovered. Computer simulations based on aggregation of two dimensional random walkers (or diffusion limited aggregation) show similar dendritic patterns in the initial stages of growth. The similarity is also reflected by their comparable fractal dimensions. For the final stages, qualitative discrepancies between the experimental and simulated patterns are discernible.

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Introduction

The phenomenon of metal oxidation is well known, and it has been the subject of research for decades. However, numerous questions concerning the initial stages of oxidation, that is, oxygen adsorption on the surface, and nucleation and growth of the oxide crystals leading to the formation of an oxide layer, are yet to be answered [Rahmel et al., 1985]. Recently, several surface science techniques (e.g., AES, ESCA, LEED, SIMS) have been applied to the study of metal oxidation processes. Researchers begin now to understand the roles of defects (dislocations, grain boundaries, step edges, etc.) and adsorbed impurities (S, P, C, etc.) in the initial stages of oxidation. On the other hand, the phenomena of non-equilibrium growth kinetics has become a subjet of increasing interest over the last decade [Sander, 1986]. Dendritic and fractal growth patterns have been studied in a number of systems, including dielectric breakdown in insulators [Niemeyer et al., 1984], two-fluid displacement in porous media [Paterson 1986], and electrolytic metal deposition [Yasuji et al., 1986]. It is therefore of both theoretical and practical interest to try to understand the kenetics of metal oxidation within the theoretical framework of non-equilibrium growth kinetics.

The development of high spatial resolution (<50 nm) scanning ion microprobes based on liquid metal ion sources [Levi-Setti et al., 1984, 1985] provides a unique tool for studying the oxidation kinetics of a metal surface on a sub-micrometer scale. This is especially true for a microprobe instrument equipped with a mass spectrometer for secondary ion mass spectrometry (SIMS), because the oxide can be imaged by using either the emitted secondary oxygen ions or metallic ions, and the entire growth process can be visualized with high spatial resolution. When the oxidation of a particular metallic element is of interest, this technique is even more advantageous because primary ions of the same element can be used for both sputter cleaning and analysis of the sample surface without introducing foreign elements to disturb the system.

We chose to study the oxidation of gallium for the following reasons. First, gallium has a very low melting point (29.78 °C) and it has a strong tendency to supercool. Therefore, it is possible to study its oxidation in both liquid and solid phases at room temperature. Second, a gallium ion beam is normally used for the operation of the scanning ion microprobe at the University of Chicago. A clean gallium surface can be prepared and analyzed *in situ* in the UHV specimen chamber of the microprobe. In this paper, we report, for the first time, the observation of dendritic oxide growth on the surface of liquid gallium. The results are compared with computer simulations based on two dimensional diffusion limited aggregation (DLA) [Witten and Sander, 1981].

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Experimental

A drop of liquid Ga, ~0.5 mm thick and covering an area of approximately 10 mm^2 on a stainless steel substrate was prepared by heating a piece of high purity (99.999%) Ga ingot to a temperature slightly above its melting point. A layer of oxide (Ga_2O_3)[Su et al., 1982], was naturally formed on the sample surface. Without appropriate seeding, the melt remains liquid after it has cooled down to room temperature (20 °C) for an indefinite time. The sample was then loaded into the UHV specimen chamber of the scanning ion microprobe, where the 40 keV focused Ga$^+$ ion beam was scanned in a raster pattern on an area of 40 x 40 μm^2 to remove the oxide layer by sputter cleaning. With a beam current of 40 pA, the typical time required for cleaning an area of this size is 40 minutes to an hour. Assuming the sputtering yield of the oxide layer is close to that of the pure Ga, which is calculated from Sigmund's theory to be 13.5 [Sigmund, 1969], one estimates the thickness of the oxide layer to be approximately 1.2 μm. (This is probably an underestimate because the sputtering yield of gallium oxide should be lower than that of Ga.)

While cleaning the sample, we monitored the signals of secondary O$^-$ and Ga$^+$ ions emitted from the surface and found that they both decreased as the oxide layer became thinner. The decrease of the O$^-$ signal can be readily understood in terms of the diminishing presence of oxide; yet the decrease in the Ga$^+$ signal is opposite to expectation because the surface Ga concentration increases as the oxide layer is removed and the underlying pure Ga exposed. In the SIMS community, this 'unexpected' result is known as the effect of oxygen enhancement on positive secondary ion emission. The mechanism of the enhancement is related to the high electron affinity of oxygen, but the details of the process are not understood [Sroubek, 1988]. The size of the enhancement is typically two to three orders of magnitude for most metallic elements. In our experimental conditions, the Ga$^+$ signal from gallium oxide was about 10^3 times stronger than that from a clean gallium surface. This dramatic effect is demonstrated by the Ga$^+$ elemental map (fig.1(a)) taken after an oxide-free window (blue) had been opened on the surface of the sample. (In this micrograph and the others to be shown later, we have adopted a pseudocolor scheme to add the intensity dimension to the two spatial dimensions; the chosen green-yellow-red color scale was inspired by the dominant colors in the seasonal cycle of tree growth, with blue for winter and no foliage, meaning here no oxide.) In terms of signal to noise ratio for locating oxide on a metal surface, the enhanced positive metallic ion signal, sometimes provides a better alternative to the O$^-$ signal because the former can be much stronger than the latter. For gallium oxide under our experimental conditions, the Ga$^+$ signal is approximatelly ten times stronger than the O$^-$ signal. Therefore, we used the Ga$^+$ signal for mapping the sites of gallium oxide throughout the experiment. Every now and then, an O$^-$ map was taken to check whether the Ga$^+$ maps described faithfully the contour of the oxide layer.

After the initial oxide distribution (fig.1(a)) was recorded over an 80 x 80 μm^2 area, the primary ion beam was zoomed back to scan over the cleaned 40x40 μm^2 window; meanwhile, high purity oxygen gas was let into the specimen chamber through a precision leak valve for the oxidation to take place. The pressure in the chamber, monitored by an ion gauge, was increased from 1 x 10^{-9} Torr to 1 x 10^{-6} Torr in a few steps over a time period of 90 minutes. Every five minutes, a Ga$^+$ map was taken to monitor the evolution of the oxide distribution. Figures 1(b) to fig. 2(f) are 'snapshots' (two minutes per image) of various stages in the growth of the oxide layer. The pressure and cumulative oxygen dose at the time when each map was taken are given in the figure captions.

Initially, the oxide grew laterally in a dendritic pattern from the four edges of the window where residual oxide protrusions existed, which acted as nucleation centers. The branches of these 'oxide trees' spanned over a large portion of the window, yet left it mostly uncovered. This dispersed dendritic pattern is reminiscent of those resulting from diffusion limited aggregation (DLA) [Witten and Sander, 1981], a topic which is to be discussed along with computer simulations of the oxide growth process. Gradually, the branches grew laterally, and also became thicker as indicated by the change of their color from green to red. To be noted is that the lateral growth of the branches seemed to take place primarily in a 'growing zone'(the green contours in fig. 1), where a thin layer of oxide has formed. Finally, the window was almost completely covered by oxide; only small islands and channels remained oxide-free.

Since oxygen molecules in the chamber collided with the sample surface randomly, the preferential growth of oxide from the edges of the window clearly indicates that the activation energy is lowered by the presence of oxide. If one assumes that oxidation takes place only when an oxygen molecular projectile lands on a site with preexisting oxide, one would expect the oxide to grow laterally in a continuous pattern, as was observed in the latter stages of the growth, rather than the dendritic pattern observed in the early stages. Therefore, the dendritic pattern must be the product of a different physical process which becomes ineffective as the growth reached the final stages. A possible model for the dendritic growth is the following: oxygen molecules were first adsorbed by the clean gallium surface without forming oxide bonds, therefore, they were 'free' to diffuse along the surface until an oxidation nucleus was encountered. In the literature, this type of process --diffuse then aggregate-- is known as diffusion limited aggregation (DLA), already referred to above. To check if this model adequately describes the growth pattern, we resort to the use of computer simulations.

Computer Simulations and Discussion

As a first approximation, we ignore the growth in thickness of the oxide layer and assume that the pattern in each stage can be represented by a two dimensional array of boolean numbers (empty or occupied.) These arrays are compared with the arrays generated by the following process, taken to represent DLA. A sticky particle is randomly landed on a 256x256 square lattice with its edges completely occupied by the same kind of particles. It then moves randomly on the lattice until another sticky particle is encountered and sticks permanently to that lattice site. This process is repeated until a certain fraction of the lattice is covered by the particles. Figures 3(a) and (b) show the simulated growth patterns covering 10% and 20% of the lattice, respectively. They are qualitatively similar to the growth

Fig.1. Secondary Ga$^+$ ion maps showing the early stages of growth of an oxide layer on a liquid gallium surface. (a) An oxide-free window created by sputtering the original oxide layer with a 40 keV gallium primary ion beam. (b) to (f) are snapshots of the oxide growth within the window, scale bar = 5 μm. The pressure (Torr) in the specimen chamber, the cumulative oxygen dose (O$_2$/cm^2), and the fractional area covered by oxide for each stage are: (b) 1x10^{-7}, 3.2x10^{16}, 11%; (c) 1x10^{-7}, 7.5x10^{16}, 21%; (d) 2x10^{-7}, 1.2x10^{17}, 34%; (e) 2x10^{-7}, 1.7x10^{17}, 37%; (f) 2x10^{-7}, 2.8x10^{17}, 43%.
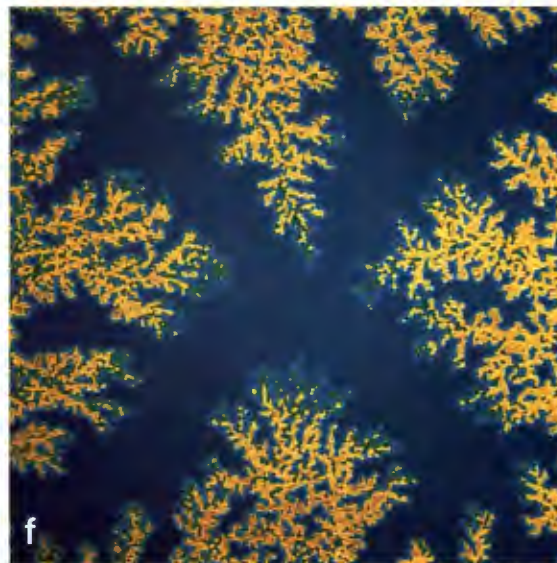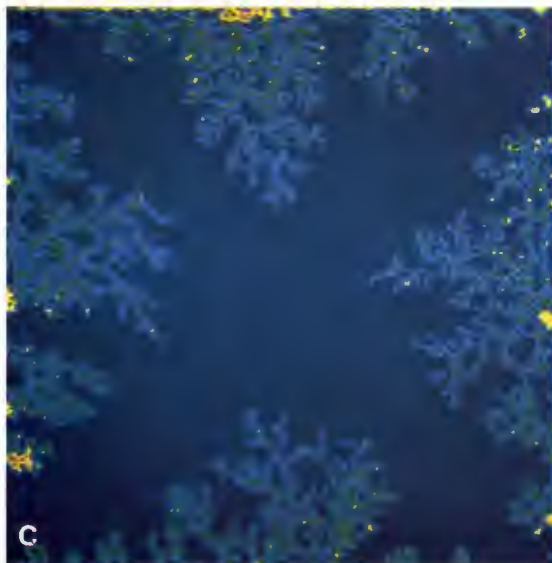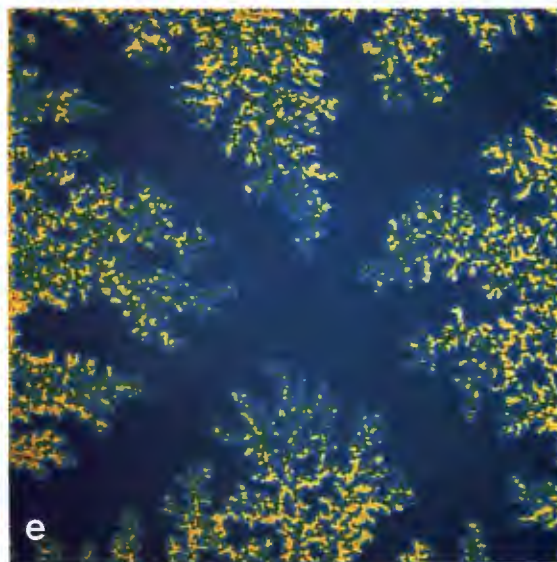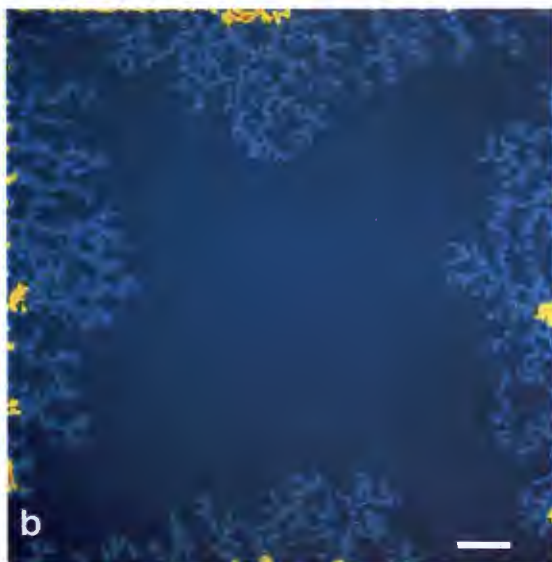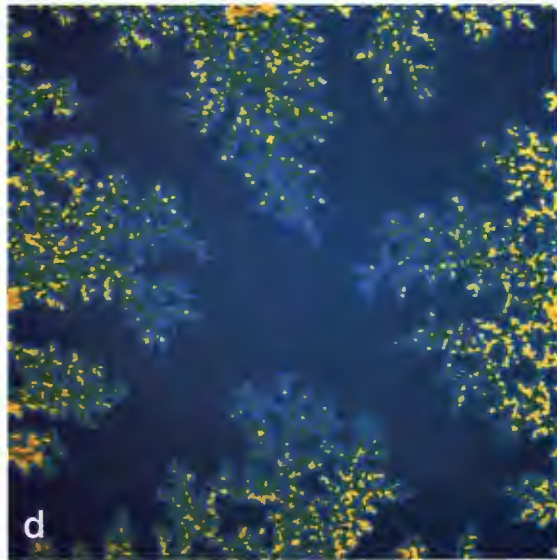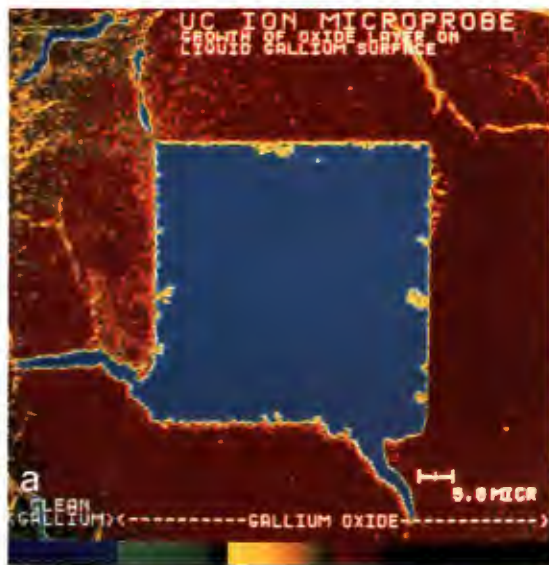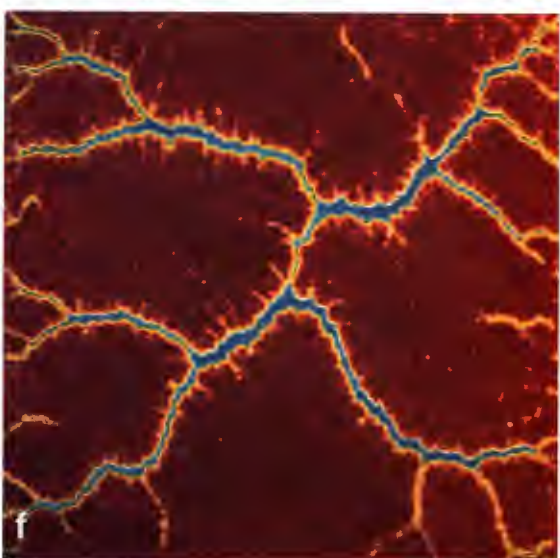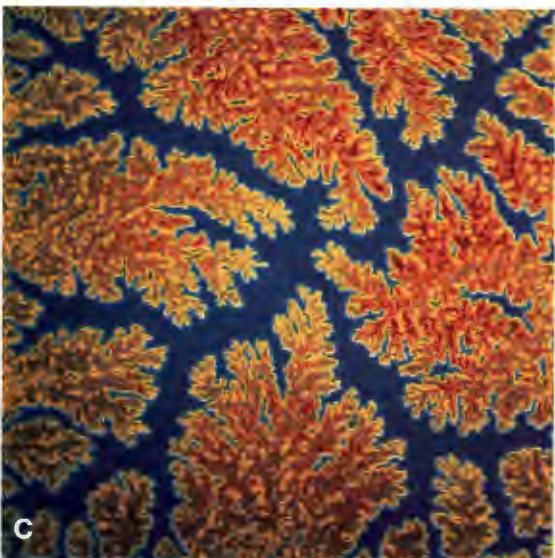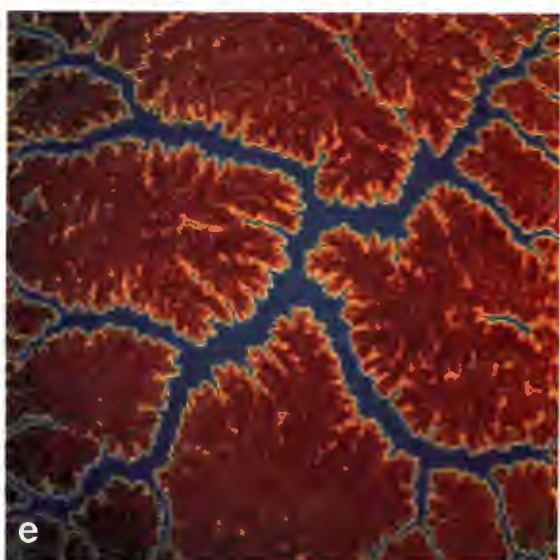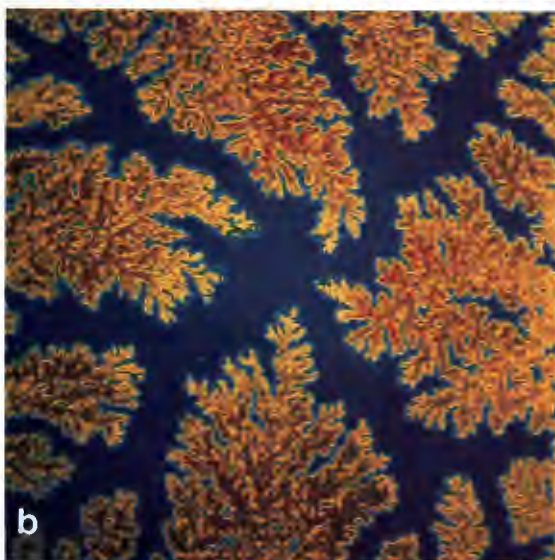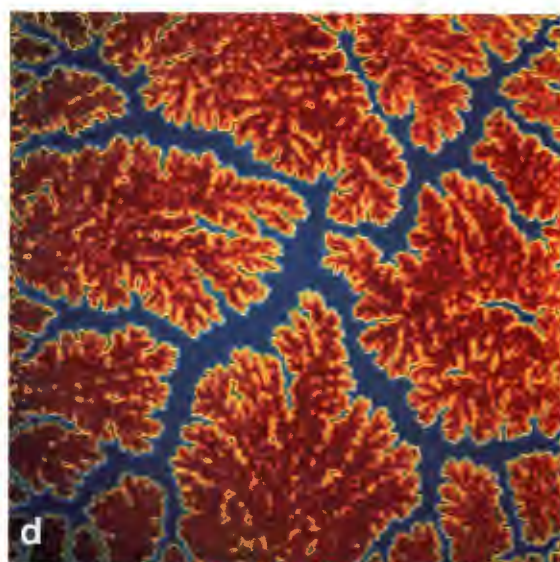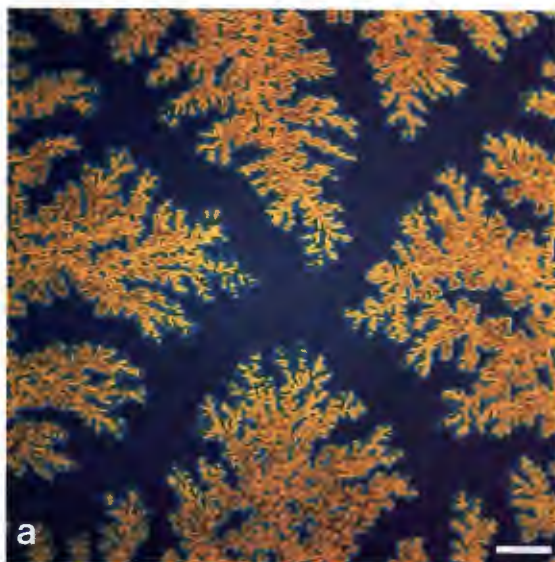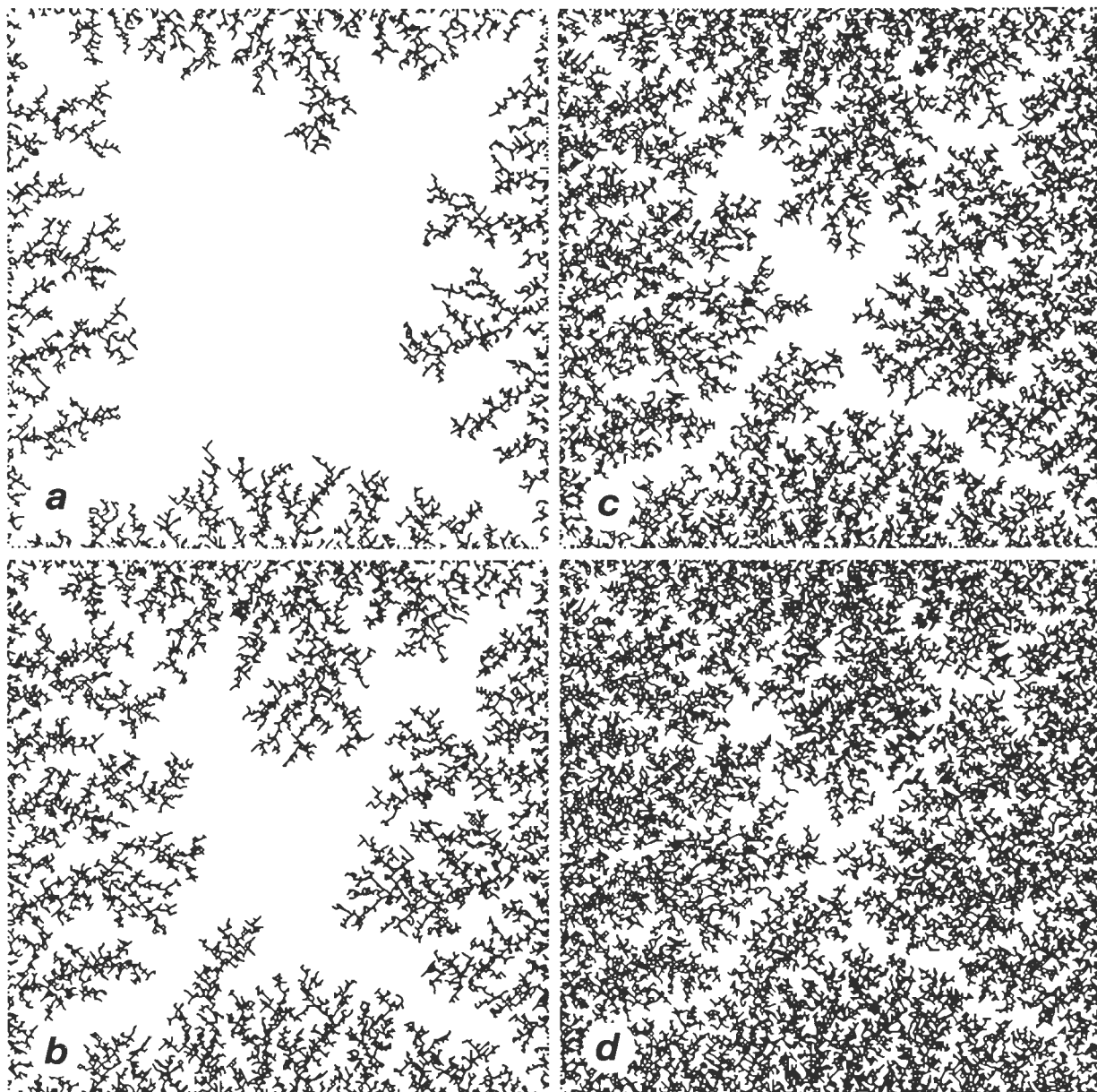
Fig.3. Computer simulations based on the aggregation of two dimensional random walkers on a 256x256 square lattice. The fractional area coverage for each stage is: (a) 10%, (b) 20%, (c) 30%, and (d) 40%.

pattern observed in the initial stages, as shown in fig. 1(b) and fig. 1(c). Figure 3(c) and (d) are the simulated patterns at 30% and 40% coverage. The branches have now spanned over almost the entire lattice yet plenty of scattered vacancies are left. This characteristic is not found in the experimental growth patterns which are more continuous at high coverages.

To compare the simulation and experiment more quantitatively, it is essential to discuss the fractal dimension of the growth patterns. The fractal dimension d of an object can be defined by the equation,

$$N=N_0(L)^{-d}, \qquad (1)$$

← —— Fig.2. Secondary Ga^+ ion maps showing the growth of an oxide layer on a liquid gallium surface, in the later stages. Scale bar = 5 μm. The pressure (Torr) in the specimen chamber, the cumulative oxygen dose (O_2/cm^2), and the fractional area covered by oxide for each stage are: (a) 4×10^{-7}, 3.9×10^{17}, 54%; (b) 4.4×10^{-7}, 6.2×10^{17}, 65%; (c) 1×10^{-6}, 8.8×10^{17}, 75%; (d) 1.2×10^{-6}, 1.2×10^{18}, 85%; (e) 1.2×10^{-6}, 1.8×10^{18}, 88%; (f) 1.2×10^{-6}, 2.4×10^{18}, 98%.
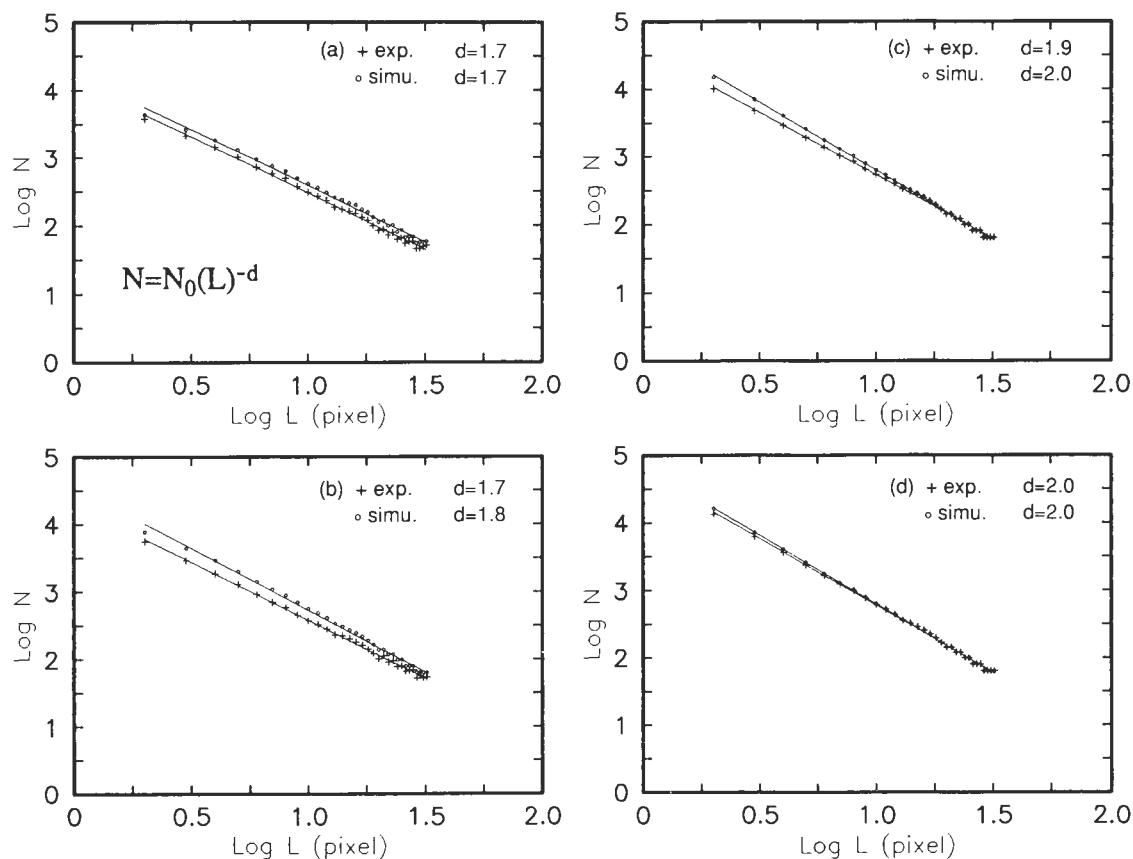
Fig. 4. Comparison of the fractal dimension d (defined in eq. 1) for the observed and simulated growth pattern at various stages. N is the number of occupied cells and L is the size of the unit cell used for partitioning the pattern. The fractional area coverage for each stage is: (a) 11% (fig. 1(b)), (b) 21%, (fig. 1(c)), (c) 54% (fig. 2(a)), and (d) 75% (fig. 2(c)).

where N is the number of cells occupied by the object when it is partitioned by a lattice with a unit size L, and N_0 is a proportional constant of no consequence. For example, the number of cells occupied by a two dimensional (d=2) object is quadrupled when the unit size of the partition lattice is divided by two.

Originally, each observed growth pattern was represented by an array of 512x512 numbers with 256 grey levels. The number of pixels was reduced to 256x256, and the number of grey levels to 2 so that the comparison between experiment and simulation could be carried out in a reasonable computation time. The fractal dimension of a pattern was calculated by, first, dividing it into cells of given size, and then, counting the number of occupied cells. This counting procedure was repeated for cells of various sizes; the results are shown in fig. 4 for the observed and simulated patterns at various fractional area coverages.

The fractal dimension of both the observed and simulated patterns grows from 1.7 to 2 as the coverage increases and the patterns become continuous. For 11% area coverage, the d-values of both patterns are the same within errors, which further confirms the adequacy of the simulation in describing the growth pattern in the initial stages. For medium area coverages (21% and 54%) , the d-values of the observed patterns are lower than those of the simulated patterns indicating a deviation of the simulation from the experiment at this stage of the growth. For high area coverages, even though both patterns approach a

d-value of 2, the simulation is clearly at variance to the observed patterns, in their qualitative appearance. The actual oxide trees have now become dense, with rounded edges, while the simulated patterns retain a lacy fabric. This qualitative difference may imply that in this case the diffusion of oxygen (or gallium) throughout the oxide layer begins to play an important role in filling-in small voids.

The effect of the primary ion bombardment on the growth pattern was examined in one run of the experiment. The ion beam was turned on only when a map was being taken. This reduced not only the sputtering of the growing oxide but also the oxygen diffusion induced by ion bombardment. Similar dendritic, yet more continuous, growth patterns were observed. We also studied the oxidation of solid gallium at room temperature. The solid surface was obtained by freezing a liquid drop. Random rather than dendritic growth patterns were observed. This might be expected because the solid surface after sputter cleaning was covered with facets and steps that trapped the surface oxygen and stopped the diffusion process.

Conclusion

For the first time, the initial stages of oxidation of a liquid Ga surface are monitored in situ down to a lateral scale of ~50 nm. Oxides grow laterally in a dendritic pattern from the edges of a preexisting gallium oxide layer on a smooth liquid

gallium surface. Similar patterns can be derived from computer simulations based on a model of diffusion limited aggregation. According to this model, the diffusion of oxygen adsorbed on the surface is believed to be the key to understanding the growth pattern in the initial stages. Gallium oxide grows instead in a random pattern on a frozen gallium surface, indicating that surface roughness following crystallization, due to grain structure, dislocations and steps, has a profound effect on the mechanism of metal oxidation. We believe these observations are not unique to the Ga system reported here. Surface diffusion can determine the nature of the oxide-growth pattern, provided the substrate is smooth enough and the temperature of the system is high enough for the adsorbed oxygen to diffuse.

Acknowledgments

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Discussion with reviewers

A. Lodding: Has the computer simulation been able to indicate any reasonable values of the effective diffusion coefficients? Do you plan to extend your studies in order to obtain a temperature dependence and to correlate with known values of diffusivities in liquid bulk gallium ?

Authors : Because the length and time scale in the computer simulation are both arbitrary, the latter does not indicate an effective diffusion coefficient in terms of real physical dimensions. We are in the process of implementing a temperature controlled sample stage. We hope to study the temperature dependence of the oxidation process in the near future.

T. A. Witten: Is it possible to infer the oxygen mobility on the liquid gallium surface from the growth rate of the oxide?

Authors : In order to measure the growth rate, we need to develop a method for measuring the thickness of the oxide layer. From the growth rate, the oxygen mobility can be inferred if the oxidation reaction proceeds at a much faster rate than the diffusion process, so that the reaction time can be neglected.

T. A. Witten: Is this mode of growth to be expected generally for metals without faceted surfaces, such as those above their roughing transition temperature or those in a glassy state?

Do the authors see any potential utility or disadvantage in this type of oxidation? Could this fine dendritic pattern of oxide on metal yield distinctive electronic or joining or catalytic properties? Is the pattern distinctive in its fineness?

Authors : We believe this mode of oxide growth occurs on any smooth surfaces to which oxygen can loosely adhere without forming strong oxide bonds until an activated site is encountered. We would like to demonstrate this mode of growth on an atomically flat solid surface and then consider the possibility of utilizing the distinctive fineness of the pattern for applications.