Cluster shape cycles during self-similar cluster growth

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In this paper we discuss an interesting feature of the system In on InP(001), i.e., that the shape of a significant number of large In clusters on the surface, formed during thermal decomposition of the compound semiconductor, undergo shape cycles between spherical and rectangular during cluster growth. Indications of repeated shape cycles are shown and a detailed theoretical discussion of the effect is given. The shape cycles are caused by enhanced substrate etching below clusters which results in the formation of square- or rectangular-shaped depressions. The depressions modify the energetic equilibrium condition governing cluster shapes such that cluster shapes follow the shape of the expanding depression for some time. We further demonstrate that the global cluster size distribution follows a self-similar behavior.

I. INTRODUCTION

Statistical self-similarity is a fundamental phenomena which dominates the late stages of phase separation. It has been first established analytically for ripening processes by Lifshitz and Slyozov.[1] Mullins generalized the self-similarity concept by applying it to other phase separation processes which are not analytically describable.[2] An example is static coalescence growth, where immobile clusters grow steadily from a supersaturation and by leaps when clusters merge upon contact. Family and Meakin observed in computer simulations that this process can be described by self-similarity,[3] and agreement with experimental observations was demonstrated for Ga clusters on GaAs(001).[4]

As self-similarity is applied to a wider range of growth phenomena, it is necessary to revisit the conditions under which it will hold. Mullins discussed these conditions, and listed among others the preservation of the cluster shape in cases where sufficient atomic diffusion in and on clusters can occur.[2] A system excluded by that condition is Pt on Al_2O_3 in oxygen atmospheres,[5] where the change in cluster shape is associated with a change in the dominant growth process. A more appropriate test for the condition of cluster shape preservation may arise if oscillating cluster shapes can be observed.

Observations of shape oscillations were recently reported by Tersoff, van der Gon, and Tromp,[6] who showed that very small Ag crystals on Si changed repeatedly between rounded and sharp corners. This effect results from a nucleation-inhibited growth mechanism, and is believed to be limited to clusters in an early stage of growth, i.e., before self-similar behavior is expected, thus in a range where Mullins' condition does not apply. We present in the following experimental data which show clusters undergoing cyclic shape changes for relatively large clusters which are in the late stage of cluster growth, where self-similar behavior can be expected. We show for our experimental system that the global cluster size distribution is in agreement with a distribution predicted for self-similar coalescence growth. Thus this system establishes an interesting test case for the relevance of shape cycles for self-similar growth behavior.

II. EXPERIMENTS

The system presented in this study is In on InP(001) at 500°C. At this temperature excess indium forms a continuous supersaturation on the surface as a result of preferential loss of P_2. The resulting large indium clusters are in the liquid state, where they have a partial spherical equilibrium shape.

Prior to insertion into the ultrahigh vacuum system, InP wafers were *ex situ* chemically cleaned. The residual oxide was flashed off thermally in the vacuum chamber (base pressure $<5\times10^{-9}$ Pa). During the experiments the samples were mounted on Mo backings and heated radiatively. The temperature was constant to within ±1°, and accurate to within ±15°. On some samples indium clusters were selectively removed from the InP surface in a solution of nitric acid and water (1:5 by volume) at 30°C. This step was taken to improve the scanning electron microscopy (SEM) analysis of the depressions.

III. RESULTS

The main results of this study are shown in Figs. 1 and 2. The paper will start with a qualitative discussion of the microscopic features visible in Figs. 1(a)–1(c), which show that single indium clusters undergo cyclic shape changes. Figure 2 is then used to show that the global cluster size distribution of the same samples is in agreement with model simulations based on the concept of self-similarity. In Sec. IV Fig. 1 is revisited to describe the driving forces, and to quantify the shape cycles of the indium clusters.

Figures 1(a), 1(b), and 1(c) show SEM micrographs of the final morphology of an InP(001) sample annealed at 500 °C for 10 min representing snapshots of the cluster evolution. The micrographs were chosen to highlight the following features: (i) about 90% of the clusters are partially spherical with diameters of up to 30 μm; and (ii) a

FIG. 1. (a)–(c) SEM micrographs of an InP(001) surface after thermal treatment at 500 °C for 10 min in ultrahigh vacuum. Morphologies and symbols are discussed in the text.

fraction of about 10% of the clusters can be associated with one or more rectangular features. These features are either clusters with a rectangular contact area to the substrate, observable from the smallest objects on the micrograph up to sizes of 30×30 μm^2 (see arrows), or are rectangularly shaped height inhomogeneities with a partially spherical cluster located in one of their corners. The rectangular areas are in a few cases cluster-free (label *R* on micrographs), but in most cases show secondary nucleation with distinct cluster size distributions of varying average cluster size (label *S*).

The observed cluster sizes in the μm-range suggest a late stage cluster growth process. In order to determine if the growth process can be described with statistical self-similarity, cluster size distributions were recorded from SEM micrographs and summarized in Fig. 2 (based on approximately 4500 analyzed clusters). The figure shows in a double-logarithmic representation the experimental cluster size distribution $N(V_c)$, with V_c the volume of the cluster. The data are compared to a numerical simulation for the case of static coalescence[3] (solid line), with an extrapolation of the simulation data to smaller cluster sizes (dashed line). The bimodal character is generally followed in the data, although the constriction is less distinct. Similar observations were reported for Ga on GaAs(001),[4] and indicate that the experimental distribution represents an earlier snapshot than the simulation curve. Very good agreement with

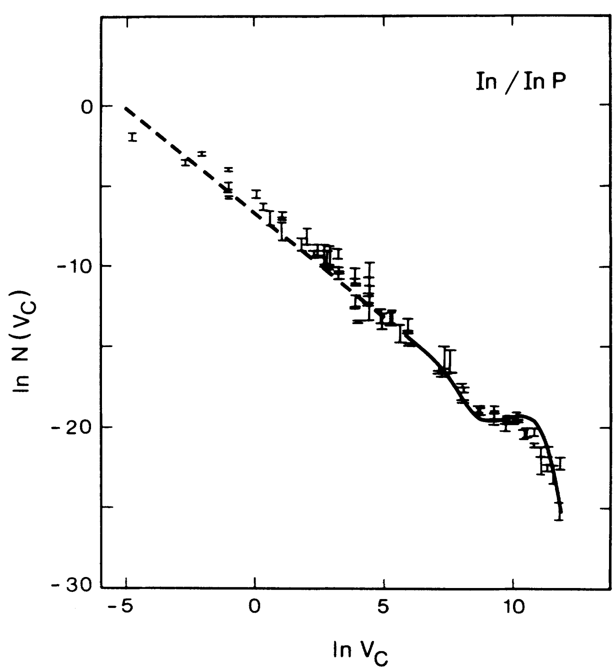

FIG. 2. Experimental cluster size distribution for In on InP(001) after annealing at 500 °C for 10 min. Data are shown in a double-logarithmic plot of the normalized number of clusters vs the volume of the clusters with comparison to a computer simulation by Family and Meakin (Ref. 3) (solid line). The power law for small clusters in the simulation is extrapolated toward smaller clusters as the experimental data cover several more orders of magnitude in size.

the theoretical value of the power-law decay exponent of $\frac{5}{3}$ is found for $N(V_c)$ at small cluster sizes. Based on the cluster size distribution our data are in agreement with a self-similar cluster growth behavior.

IV. DESCRIPTION OF MODEL

We want first to reinvestigate the question of the fraction of clusters associated with nonspherical morphologies in Figs. 1(a)–1(c). The apparent fraction as stated above (about 10%) represents a lower limit for two reasons. (i) It is evident from Fig. 1(a) (see arrows) that rectangular shapes are associated with clusters of all sizes, but the resolution limit of the SEM has the consequence that the shape of smaller clusters becomes unresolved before the cluster as such would become invisible. (ii) More fundamental is the value of the fraction influenced by processes subsequent to the formation of a rectangular depression. As a result it is difficult to detect "older" rectangular areas as the boundary lines disappear as new clusters grow over them. We therefore estimate an actual fraction of about 20% of clusters to be associated with rectangular structures. Another consequence of the last argument is that we rarely observe more than one overlapping rectangular area associated with the same cluster. However, such cases are clearly visible, e.g., in Fig. 1(b) (see cluster *P* and associated depressions 1 and 2).

Based on these observations we can evaluate various models for the dynamics of single indium clusters: (a) all clusters have one shape, the other shape is an artifact of the quenching prior to the SEM analysis; (b) coexistence of rectangular and spherical clusters without transitions between the shapes; (c) a single transition from spherical to rectangular in a certain size range (e.g., about 10-μm cluster diameter); (d) a single shape cycle; and (e) a repeating shape cycle (shape oscillations).

To evaluate these models a method for timing the age of structures in the micrographs relative to the time of the temperature quench, i.e., the end of the experiment, is needed. The most elegant approach would certainly be a real-time recording of the evolution of the morphology. However, a straightforward approach, e.g., using an ultrahigh vacuum system SEM with video capability, has to be considered carefully, as we observe frequently that the reported structures as well as the InP substrate itself are rather sensitive to electron bombardment during microscopic analysis. An indirect approach which does not interfere with the ongoing evolution process is a univocal dating procedure of morphological properties associated with the primary structure that is to be dated. This is possible for regions where clusters undergo detachment from the rectangular depressions. This is based on the fact that immediately after detachment secondary nucleation occurs, and the secondary nuclei start to grow due to the continuous increase of indium monomers on the surface. A detailed quantitative discussion is presented elsewhere,[7] and is only briefly outlined here to show how the relative age of structures can be determined.

In areas which are exposed after the relaxation of a cluster, an indium supersaturation will build up over a short period followed by a sudden start of nucleation. The supersaturation then decreases through diffusional loss to the nuclei and reaches a steady-state value. Nuclei also grow due to enhanced etching of the substrate below the clusters, as discussed in Sec. V. Cluster growth by diffusion and etching continues until the radii of clusters are large enough to overlap, and coalescence starts to dominate. The cluster growth rate is quantified for the transitional growth stage of the secondary nuclei, assuming that no significant free-adatom concentration level builds up. If diffusional processes dominate, the rate of increase of atoms in a cluster is proportional to the area which is surrounded by the lines where the adatom concentration gradient vanishes times the P desorption rate constant from InP. We find[7]

$$r_i^3(t)-r_i^3(t_0)=\frac{v_M S_{i,\inf}\kappa_{\mathrm{InP}}}{\alpha}(t-t_0)\ . \tag{1}$$

v_M is the atomic volume of indium, κ_{InP} is the rate constant for P desorption from InP and α is a geometric constant defined by the volume of the cluster ($V_{\mathrm{cluster}}=\alpha r^3$). Therefore the third power of the radius of the cluster is proportional to time, and scales with the area from which the cluster takes up adatoms, $S_{i,\inf}$. An absolute time scale can only roughly be determined, as κ_{InP} is usually not well known. However, for most cases a relative comparison of the age of depressions is sufficient, since the large number of such areas on the same sample represents all different morphologies during the early stage. In these cases the rate factor cancels, resulting in

$$\frac{t_1}{t_2}=\frac{r_{i=1}^3(t_1)}{r_{i=2}^3(t_2)}\frac{S_{i=2,\inf}}{S_{i=1,\inf}}\ . \tag{2}$$

Thus the age of a structure can be associated with the relative size of clusters, as the size is a monotonic function of time for growth of secondary nuclei. This is also true if the etching process below the cluster dominates the increase of indium in the cluster.[7]

With such a dating ability we can conclude that the detachment of clusters from rectangular depressions in Figs. 1(a)–1(c) occurred at different times before the temperature quench. Since plain depressions (at the resolution limit of the SEM) are observed [*R* in Figs. 1(a) and 1(c)], only the formation of these structures could occur during the temperature quench. However, most structures show visible secondary nucleation and must have formed at different times before the quench.

With these additional observations we discuss the different models proposed above: Cases where all clusters have the same shape with changes only during the quench (a), and a coexistence of two separate sets of cluster shapes without transitions (b) can be ruled out due to the observation of transitions before the quench as indicated by visible secondary nucleation in the exposed depressions. A single transition in a certain size range (c) can be excluded since transitions in both directions are observed, and the presence of secondary nucleation again excludes the restriction of transitions to the quench period. The remaining models are (d) and (e), with the difference of either single or multiple shape cycles per cluster. The observation of more than one depression associated with the same cluster [Fig. 1(b)] is suggestive that clusters undergo repeated shape cycles. With a size-independent shape cycle for the clusters established, and a frequency of these events such that about 20% of the clusters are affected in a short time interval before the quench, multiple shape cycles are also expected statistically.

V. QUANTIFICATION OF CLUSTER SHAPE CYCLES

The remaining discussion in this paper describes step by step the shape cycle of single clusters. We start with the formation of subsurface depressions below each cluster. This is the major driving force for shape changes. The shape change is then analyzed first for the formation of rectangular shapes from initially partial spheres. The rectangular shapes originate from preferential crystallographic etching behavior during the formation of the subsurface depressions. Then we will show that the cluster on top of a depression follows the development of a rectangular-based shape to a point where further elongation of the rectangular base becomes energetically unfavored. At this point the cluster will partially detach from the depression and retract to an equilibrium spherical shape. At that time the evolution of the depression stops, and the shape cycle repeats.

Subsurface depressions occur commonly in several metal/semiconductor systems for III-V compound semiconductors, as highlighted in Figs. 3(a) and 3(b) for In/InP. The rectangular depression has a rather shallow depth of about 0.25 μm as compared to the radius of the cluster of 10 μm. Figure 3(b) is a SEM micrograph of the same sample after indium has been chemically removed. It is obvious that depressions occur in two distinct shapes, round and rectangular. From the contrast at the edges it appears that the rectangular depressions are deeper than circular depressions, cross-sectional SEM micrographs show that rectangular depressions are on average 2.5 times deeper. The origin of depressions has been studied extensively for the system Ga on GaAs(001).[8] It has been shown that it is the result of the competition between two processes of group-V component loss; (i) bulk diffusion of the group-V element through the semiconductor and desorption, and (ii) dissolution of the semiconductor into the metal clusters, and diffusion of the group-V element in this cluster to the surface and desorption. The required thermodynamic data for this comparison are available for InP.[9] Using the preexponential factor $D_0=7\times10^{10}$ cm^2 s^{-1}, and the activation energy $E_d=5.65$ eV, an average rate of loss for the duration of the experiment at 500°C of 8×10^7 P atoms/cm^2 s is estimated, with an initially higher rate that decreases fast as P has to diffuse from larger depths. For loss through the cluster the corresponding diffusion of P in In is much faster ($D_0=3.7\times10^{-3}$ cm^2 s^{-1}, $E_d=0.33$ eV, with diffusion lengths of 0.25 cm at 500 °C for 10 min). The rate limiting step in this process, however, is the desorption of P_2 from the cluster. We estimate the desorption rate from equilibrium data for the vapor pressure of P_2, the dominant vapor species, along the liquidus line for an In-rich In/P system. Neglecting an adsorption barrier, the desorption rate is calculated from $p_{eq}/(2\pi MkT)^{1/2}$,[10] with p_{eq} the equilibrium partial vapor pressure of P_2 at $T=500$ °C, and M the molecular mass of P_2. Using the solubility of P in In(at 500 °C) as 7×10^{-4} at. %, and a vapor pressure $p_{eq}(500\,°C)$ of 1×10^{-9} atm, we find a desorption rate of 2.4×10^{14} P/cm^2 s. Thus P loss is faster from areas beneath clusters. This explains the creation of subcluster depressions.

The next step is to show that the dissolution of the substrate occurs initially toward forming rectangular-shaped depressions. Only a brief discussion is needed, as the formation of rectangular etch pits is commonly observed for these semiconductors, e.g., under hydrogen overpressure.[11] The etching rate ratio for the forming sidewalls,

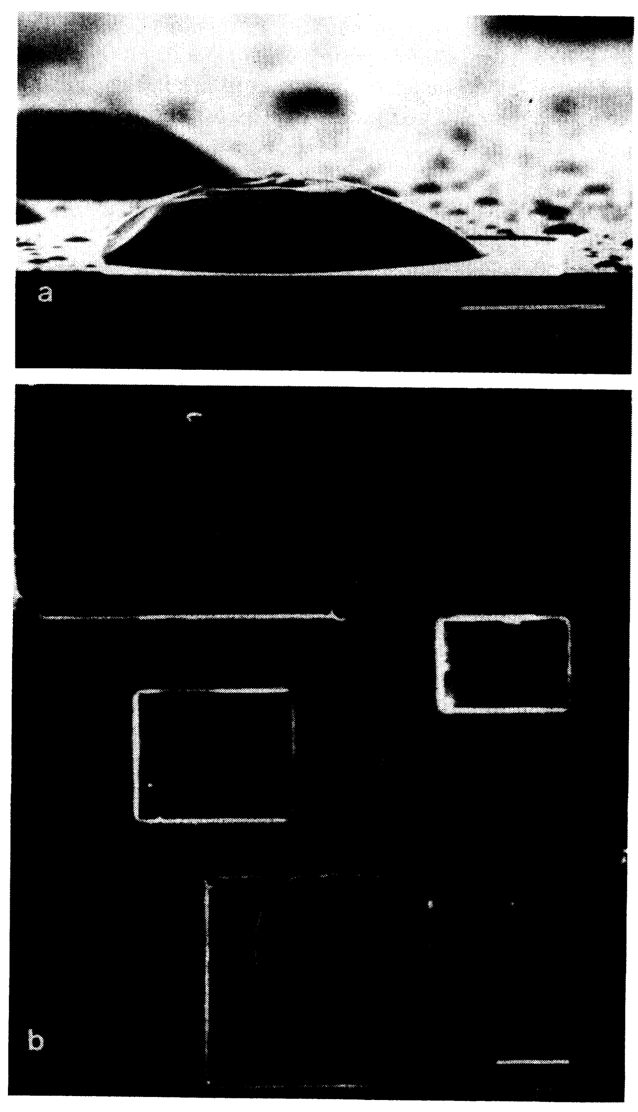

FIG. 3. (a) SEM cross-sectional micrograph of an In cluster located in a substrate depression. The contact angle with the flat InP surface is about 50°. (b) InP surface after thermal treatment and subsequent chemical removal of In metal. Note the correlation between the occurrence of rectangular and round depressions.

(111)A and (111)B, is roughly 2:1, resulting in a corresponding length ratio of the rectangular edges. From structures observed after a long etching process, we know that the (111) and (100) planes are more etch resistant than other planes. Thus the evolution of the depressions in our study is as follows. For a spherical cluster on top of the surface, etching starts vertical to the surface, initially forming a round depression. As the cluster erodes the substrate, side faces in the depression become exposed. As their areas become significant, etching of these planes will increasingly contribute to the P saturation of the In cluster, and the etching of the ground plane will decrease as it has a lower etch rate. On the side areas the etching rates between different facets will compete, and facets other than (111) disappear. The cluster must steadily accommodate for changes away from its round, top-of-the-surface equilibrium shape. Thus we initially observe the formation of square depressions. When the square base is reached, etching on (111) and (100) planes accelerates (as no faster etching planes are left), resulting in the above-mentioned larger depths for the rectangular holes. Also the (111)A – (111)B aspect ratio approaches its equilibrium value. This value is not reached, however, as most depressions have a sidewall length ratio between 1.0 and 1.2.

This latter result is due to the last step of each shape cycle, where the cluster retracts to a spherical shape. This process is driven by the energetic changes of a cluster with size and shape. The energy for a partially submerged cluster can be quantified using surface tension values for In/vacuum $\gamma_{cv}=0.515$ Jm^{-2},[12] InP/vacuum $\gamma_{sv}=0.33$ Jm^{-2},[13] and the In/InP interface γ_{cs}. Based on a contact angle of 50° [Fig. 3(a)], and using the Young-Dupré equation, we find $\gamma_{cs} \ll \gamma_{cv}, \gamma_{sv}$. These values show that the formation of submerged interfaces at the expense of In/vacuum surfaces is energetically favored, i.e., the formation of the depression is initially both kinetically and energetically favored. As the etching rate of the sidewalls increases at the expense of etching normal to the surface, the cluster stretches its surface. This stretching of the cluster surface eventually results in a net increase of cluster surface as compared to a partial spherical cluster of the same volume. Such unstable clusters will retract to a spherical shape, thus completing one cycle of the shape oscillations observed in the cluster growth experiments. This latter point has been quantified in model calculations based on the thermodynamic data discussed in this paper and the use of a simplified shape for the cluster above square or rectangular depressions (two intersecting cylinders or pyramid). Detachment is predicted for ratios from 1.05:1 to 1.15:1 depending on the relative etching rates of the different faces of the depression walls. These ratios are lower than the experimentally observed value, and are mainly attributed to the choice of shape for the cluster which results in a larger cluster surface area than the real shape.

VI. CONCLUSIONS

We have shown that single indium clusters on InP change their shape in a cyclic manner due to the formation of subsurface volume fractions. Rectangular shapes are favored over the spherical equilibrium liquid droplet shape due to formation of the depression. However, as the etching process proceeds, the In/vacuum surface increases. The size of the depression continues to increase until eventually detaching from the rectangularly based depression is favored energetically, and the cluster retracts to the spherical equilibrium shape. These shape change cycles take place as the global cluster size distribution develops in a coalescence growth mode, which is in agreement with model simulations based on the concept of self-similarity.

The observation of size-independent shape cycles of a significant number (20% in our study) of clusters growing apparently in a self-similar fashion on a surface establishes an interesting test case for theoretical predictions. A qualitative observation is that the fraction of clusters associated with rectangular shapes may increase with temperature, but such measurements have to be considered cautiously, as the temperature range over which the experiment can be done is narrow. On the theoretical side it would be interesting to see whether these observations establish a contradiction to Mullins' condition (that cluster shapes have to be preserved during self-similar growth if sufficient atomic diffusion is possible) or whether the required etching process creates a modification which could result in a new set of conditions.

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[1] I. M. Lifshitz and V. V. Slyozov, J. Phys. Chem. Solids **19**, 35 (1961); Zh. Eksp. Teor. Fiz. **35**, 479 (1958) [Sov. Phys. JETP **35**, 331 (1959)].

[2] W. W. Mullins, J. Appl. Phys. **59**, 1341 (1986).

[3] F. Family and P. Meakin, Phys. Rev. Lett. **61**, 428 (1988).

[4] M. Zinke-Allmang, L. C. Feldman, and W. van Saarloos, Phys. Rev. Lett. **68**, 2358 (1992).

[5] J. T. Wetzel, L. D. Roth, and J. K. Tien, Acta Metall. **32**, 1573 (1984).

[6] J. Tersoff, A. W. Denier van der Gon, and R. M. Tromp, Phys. Rev. Lett. **70**, 1143 (1993).

[7] M. Zinke-Allmang, S. C. Puddephatt and T. D. Lowes, in *Proceedings of SPIE's OE/LASE'94 Conference on "Epitaxial Growth Processes", Los Angeles, California, 1994*, edited by C. Palmstrøm (SPIE, Bellingham, WA, in press).

[8] T. D. Lowes and M. Zinke-Allmang, J. Appl. Phys. **73**, 4937 (1993).

[9] H. C. Casey and G. L. Pearson, in *Point Defects in Semiconduc-*

tors, edited by J. H. Crawford and L. M. Slifkin (Plenum, New York, 1975), Vol. 2, p. 224ff; Diffusion Defect Data **21**, 163 (1980); **44/45**, 187 (1986); H. Jacob and G. Müller, in *Semiconductors: Technology of III-V, II-VI, and Non-tetrahedrally Bonded Compounds,* edited by M. Schulz and H. Weiss, Landolt-Bornstein, New Series, Group III, Vol. 17, Pt. d (Springer, Heidelberg, 1984), pp. 323 and 329.

[10]I. Estermann, Z. Elektrochem. **31**, 441 (1925).

[11]W. Y. Lum and A. R. Clawson, J. Appl. Phys. **50**, 5296 (1979).

[12]L. E. Murr, *Interfacial Phenomena in Metals and Alloys* (Addison-Wesley, Reading, PA, 1975), p. 101ff; *CRC Handbook of Chemistry and Physics,* edited by R. C. Weast and M. J. Astle (Chemical Rubber Company, Boca Raton, FL, 1979), p. F-31.

[13]A. S. Popov and L. Demberel, Kristall. Technik. **12**, 1167 (1977).

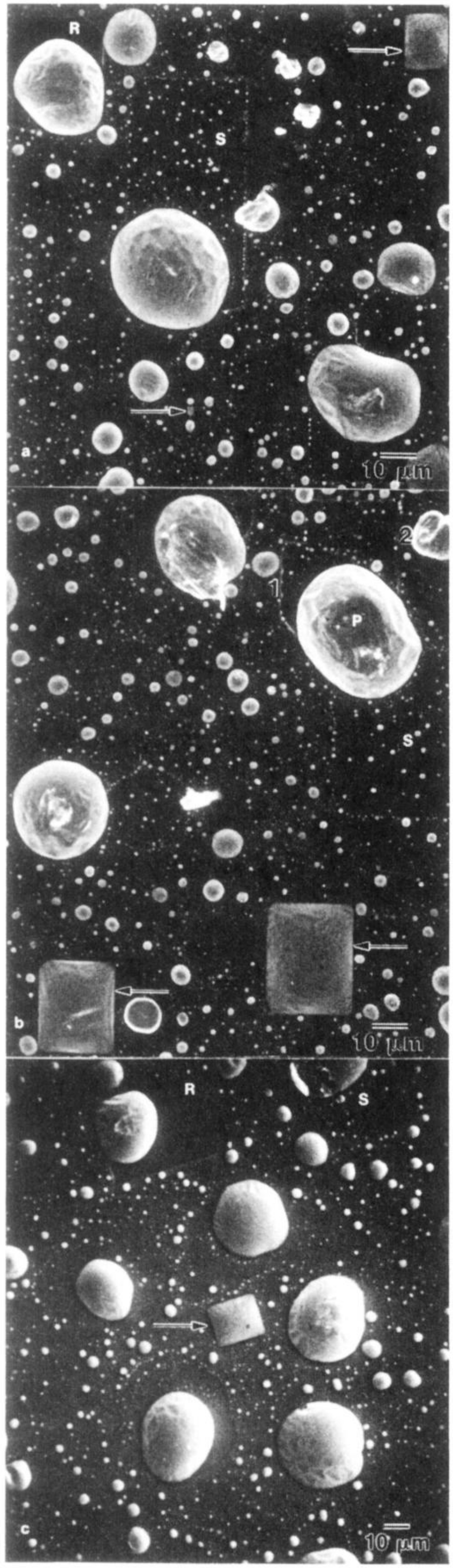

FIG. 1. (a)–(c) SEM micrographs of an InP(001) surface after thermal treatment at 500 °C for 10 min in ultrahigh vacuum. Morphologies and symbols are discussed in the text.

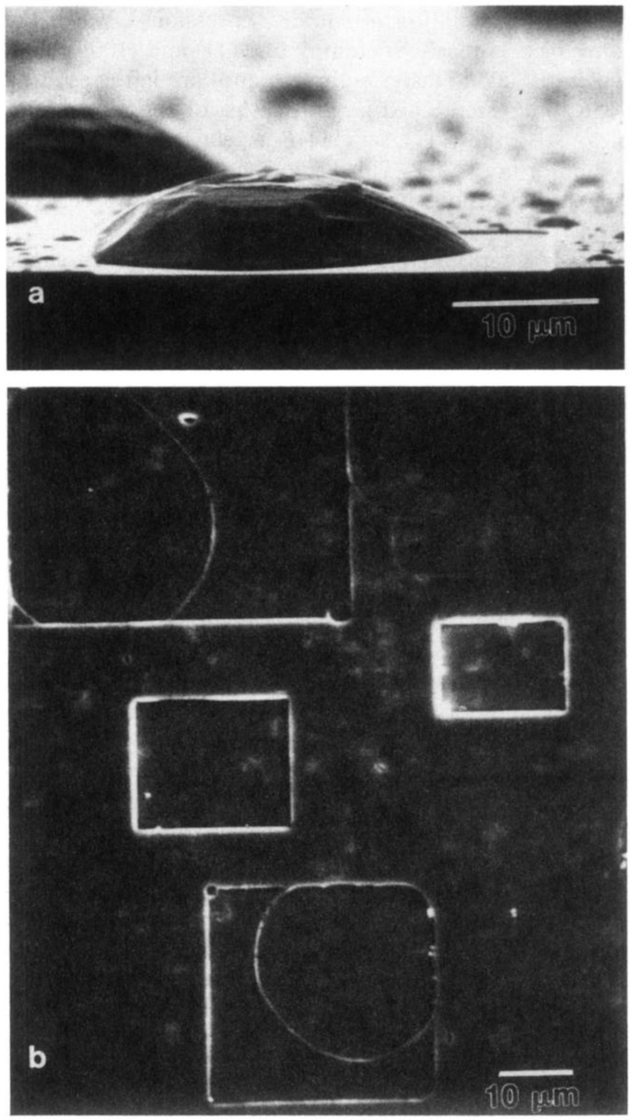

FIG. 3. (a) SEM cross-sectional micrograph of an In cluster located in a substrate depression. The contact angle with the flat InP surface is about 50°. (b) InP surface after thermal treatment and subsequent chemical removal of In metal. Note the correlation between the occurrence of rectangular and round depressions.