Reports

Vaporization of Solids: Evidence for a Zipper Mechanism in the Retarded Vaporization of Arsenic

Abstract. *Recent observations indicate that the rate of evaporation of elemental arsenic into a vacuum is determined by the rate of formation, at screw dislocations, of kinks in ledges of molecular height. Once formed, a kink advances along the ledge, which makes a continuous spiral ramp outward from the dislocation, until the ledge terminates. A kink advances by releasing* As_4 *molecules from the ledge. A given kink releases almost* 10^6 As_4 *molecules before the next kink is initiated.*

We report here recent observations which indicate that the evaporation of elemental arsenic proceeds by a "zipper," or unraveling, mechanism. This mechanism implies that the overall rate of vaporization is determined by a process, kink initiation, which takes place infrequently at low-density surface defects, that is, at emergent screw dislocations. Although zipper mechanisms are common in the degradation and other reactions of natural and synthetic high polymers, we are not aware of previous indications that such a chain reaction may occur on a crystal surface. Our observations reemphasize the potential importance of dislocations and related defects (such as ledges, kinks, and impurities segregated along dislocation lines) in chemical reactions occurring at solid surfaces.

The vaporization of solids has received continuing attention (*1–3*) both because evaporation illuminates the atomistic paths by which molecules are detached from solids, and because evaporation and condensation play important roles in many technological processes. The vacuum evaporation rates of many solids ("normal" solids) are given by the rate at which vapor particles collide with the surface when the solid is in equilibrium with its vapor. However, for those solids in which gaseous molecules as such do not exist in the solid lattice the rate of evaporation into a vacuum may be slower; that is, they may have vaporization coefficients α_v less than unity. The evaporation rates of "normal" solids, $\alpha_v \simeq 1$, are determined by the rate at which gas molecules desorb from the surface. However, retarded vaporization rates, $\alpha_v < 1$, may be determined by certain processes that take place at the surface prior to desorption.

The vaporization of gaseous As_4 from arsenic single-crystal cleavage surfaces, $\alpha_v = 8 \times 10^{-5}$ at 550 K (*4*), has been studied extensively as a prototype of retarded vaporization (*4–8*). Earlier work has shown that the evaporation of As(111) cleavage faces is accompanied by the formation of trigonally symmetric etch pits at dislocations (*5–8*). The shallow slope of about 11° between the pit sides and the cleavage surface indicates that the pit sides are composed of (111) terraces separated by ledges (*5*) of monomolecular height (*8*). As vaporization proceeds, pits grow until the surface is covered by intersecting pit sides, at which time the evaporation rate becomes constant and independent of pit density (*5*). During the initial vaporization period, before pits intersect, the evaporation rate is proportional to the area of surface covered by pits and increases parabolically with time, since the pits grow outward at a constant rate (*5*). Measurements of vaporization rate and surface morphology during the initial stages of vaporization show that the evaporation rate is proportional to the total length of ledge on the surface (*3, 5, 6*). Once formed at a ledge, gaslike As_4 molecules appear to migrate relatively freely on the terraced surface before desorbing in thermal equilibrium with the surface (*7–9*).

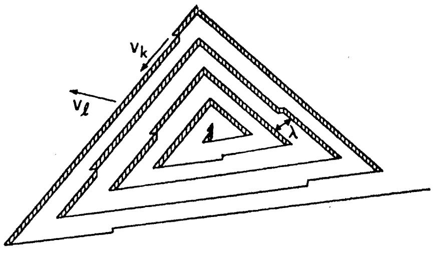

Fig. 1. Schematic diagram of a triangular vaporization pit formed at a screw dislocation, showing monomolecular ledges and kinks. In the zipper mechanism, kinks form at the ledge origin.

The observed dependence of vaporization rate upon ledge length is consistent with two types of mechanisms. In the type of mechanism normally assumed (*1–6*) the rate-determining step occurs more or less randomly along the ledge. An alternative is a zipper mechanism, in which the rate of vaporization is determined by the rate at which kinks form at the pit center. [A kink is a jog in the ledge such that parallel ledge sections which meet at the kink are displaced from one another, by one molecular unit, in the surface direction perpendicular to the ledge (*1–3*).] This mechanism requires that the pit appear at a screw dislocation so that the ledge forms a continuous spiral ramp originating at the pit center (*2, 3*) (see Fig. 1). Once a kink is initiated at the spiral ledge origin, consecutive atomic rearrangements to form As_4 molecules occur rapidly at the kink, causing the kink to advance along the ledge, like a slider on a zipper, releasing As_4 molecules proportional in number to the length of ledge which the kink traverses.

In an effort to distinguish between these two types of mechanisms, we have observed (primarily by time-lapse

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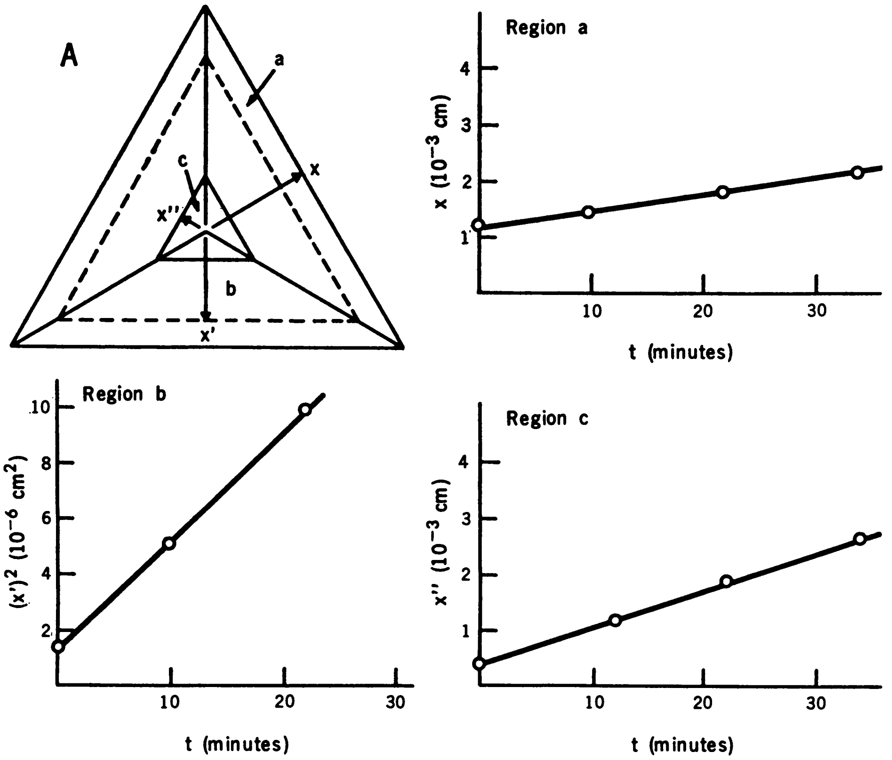

Fig. 2. (A) Schematic diagram of a triangular pit after a change in the kink initiation rate (see text). The three graphs show typical measured dimensions of regions a, b, and c as a function of time on an evaporating arsenic surface; $(x')^2$ is plotted for region b, whereas x is plotted for region a and x'' is plotted for region c. The graphs are from different pits at 566 K.

microinterferometry of evaporating arsenic single crystals, purity > 99.9999 percent) that:

1) All As(111) vaporization pits are trigonally symmetric, which implies that they result from screw dislocations along the [111] direction (*10*). In contrast, many asymmetric pits form upon chemical etching (*10*).

2) Vaporization pits have a crystallographic orientation different from that of chemical etch pits, an indication of a different atomic ledge structure. The crystal structure and the low-energy electron diffraction observations indicating no surface reconstruction (*8, 11*) show that, in vaporization pits, six more next-nearest-neighbor bonds (6 kcal per bond) (*12*) have to be broken to remove As_4 units from straight ledge than from kink positions. The opposite is true in chemical etch pits.

3) Although minor impurities in the solid do not noticeably affect the formation of chemical etch pits, they readily inactivate dislocations for evaporation, probably by segregating along dislocation lines. Impurities also can lead to changes in pit morphology, ledge spacing, and ledge advancement rate. Such changes, which are highly correlated with each other, always start at the pit center.

4) If a dislocation line bends to a new position, the original vaporization pit stops growing and a new pit appears in the new location. When vaporization pits stop advancing into arsenic crystals, they remain pyramidal and do not become flat-bottomed, as a result of outward ledge motion, in contrast to the behavior of dislocation etch pits in other systems (*13*). Flat-bottomed pits appear only in the shallow, damaged surface layer observed during the initial vaporization of freshly cleaved, unannealed crystals: they grow at a rate in the range 1/4 to 1/14 of the growth rate of normal pyramidal pits.

5) Tester, Herrick, and Ellis (*8*) report that a vicinal (stepped) arsenic surface cut at the same angle to (111) as the sides of typical evaporation pits rearranges further (at unidentified sites) upon evaporation, rather than evaporating from the ledges already on the surface. Low-index crystal faces other than (111) also rearrange extensively upon vaporization. The rate of vaporization from these other planes can be predicted from the (111) rate by projection of (111) vaporization pits upon the plane of interest (*14*).

6) When two pits intersect, the pit growth rate and pit slope sometimes change at the point of intersection. When this happens, the effects of intersection are seen equally in all three sides of the triangular pit, not just in the intersected side.

All of the results cited above are indicative of, and consistent with, the zipper mechanism. However, if the rate-determining process were to take place randomly along the ledge, then crystal edges, vicinal surfaces, edge dislocations, and vacancy clusters could, like screw dislocations, be ledge sources. Once formed, a ledge would release As_4 units until it was destroyed, contrary to the observations presented here. In the zipper mechanism the kinks are initiated at screw dislocations. They move along a given ledge in the same direction and do not annihilate each other. If the ledge is perturbed in some way, all of the spiral ledge beyond the point of perturbation may be affected. When pits intersect, it appears that the ledges often match up smoothly, as has been observed directly on NaCl (*15*).

The zipper mechanism has further interesting implications concerning the effect of impurities on evaporation rate and surface morphology which are in agreement with the experimental results. Some of these are discussed below.

If the rate r_k of kink initiation at the ledge origin is changed suddenly by an impurity at the dislocation core,

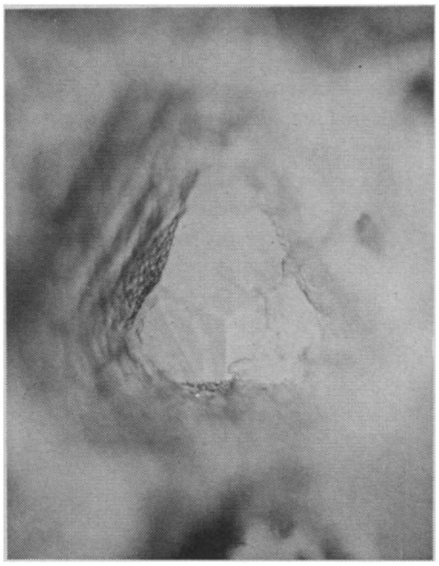

Fig. 3. Interference contrast photomicrograph of a pit 1.2×10^{-3} cm deep on an arsenic single-crystal surface (× 510). The crystal was vaporized in a vacuum after 40 hours of exposure to an oxygen pressure of 8×10^{-5} torr at 558 K. Catalysis by oxygen increases the evaporation rate of As_4 over that of unannealed crystals by a factor of 5.

the "zipper" model predicts that the resulting change in kink density along the ledge will, after a time, give rise to three regions in the pit: region a, the old ledge not yet reached by the new kink density; region b, the ledge originally formed by kinks initiated at the old rate but which has since been traversed by kinks initiated at the new rate; and region c, the new ledge formed after the change in the kink initiation rate.

The mechanism indicates that pit regions a and c will have constant slope (ledge-spacing) and will move outward at a constant rate [dx/dt or dx''/dt, see the pit diagram (Fig. 2A)] equal to the ledge velocity, v_l or v_l'. However, region b, which is unique to the zipper mechanism, will move outward more rapidly, with a rate dependent upon the kink velocity v_k along the ledge. One can calculate the characteristics of region b on the assumption that the only effect that an impurity would have on triangular pits is a discontinuous change in r_k. (In this model we neglect small changes in pit shape caused by a change in r_k.) The outer edge of region b (at a distance x' from the pit center) will move at a decreasing rate because the time, $\delta t = 6\sqrt{3}\, x'/v_k$, required for a kink to make one trip around the pit increases farther out from the pit center:

$$\frac{dx'}{dt} = \frac{\lambda v_k}{6\sqrt{3}\, x'} \qquad (1)$$

where λ is the original, region a, ledge spacing. The ledge spacing λ' at the outer edge of region b will be

$$\lambda' = \lambda + \frac{\sqrt{3}\, x' \,(v_l - v_l')}{v_k} \qquad (2)$$

Thus, the zipper mechanism implies that impurity perturbations lead to pit regions of variable slope which sweep out at velocities greater than the ledge velocities. This is observed upon vaporization of arsenic crystals. Measurements of the rate of growth of regions a, b, and c, as illustrated in Fig. 2, are in accord with the model presented in the preceding paragraph. For typical triangular pits, $dx/dt = v_l = 5 \times 10^{-7}$ cm sec^{-1} at 566 K. This corresponds to a kink initiation rate of $r_k = v_l/d_k = 8$ kinks per second per dislocation, where d_k is the distance a ledge moves when a kink passes a given point. The vaporization rate at 566 K is 1×10^{14} molecule cm^{-2} sec^{-1} (*4*). The kink velocity v_k can be computed from the slope of a plot of $(x')^2$ as a function of time for region b, such as that in Fig. 2, via Eq. 1. At 566 K, $v_k = 0.3$ cm sec^{-1}. From this we calculate that the rate at which As_4 units are released from a kink is 7×10^6 molecules per second per kink and that the average length of the spiral ledge between kinks is 3×10^6 Å.

The zipper mechanism further implies that, if the rate of kink initiation is increased markedly, $v_l' > v_l$, then, at some distance $x'_{\rm lim}$ from the pit center, $\lambda' = 0$ in Eq. 2. At $x'_{\rm lim}$, ledges pile up and the pit will bore a hole through the crystal, because ledges moving at the original rate are caught by ledges moving at the increased rate before the kinks have time to traverse the circumference of the pit. This is observed when arsenic vaporization is catalyzed by dissolved oxygen or neutron bombardment (Fig. 3). Assuming that catalysis causes v_l' to be equal to $9v_l$ in deep pits (*6*), we compute $x'_{\rm lim} = 1 \times 10^{-3}$ cm from the numbers above, a result in agreement with the observed dimensions of deep pits. It appears that many of the features of arsenic vaporization catalysis (*6*) can be explained if catalysis involves vacancy diffusion to dislocation cores, where the vacancies increase the rate of kink initiation five- to tenfold.

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Laurentide Ice Sheet Meltwater Recorded in Gulf of Mexico Deep-Sea Cores

Abstract. *Oxygen isotopic measurements in three Late Quaternary deep-sea cores from the Gulf of Mexico record a major anomaly between about 15,000 and 12,000 years ago superimposed on a more characteristic oceanic oxygen isotopic curve. This resulted from major influx of isotopically light glacial meltwater via the Mississippi River from the disintegrating Late Wisconsin Laurentide Ice Sheet 2000 kilometers to the north.*

During the last 2.6 million years the northern North American continent has been periodically covered by immense ice sheets (*1*). The Laurentide Ice Sheet advanced to its Late Wisconsin maximum about 18,000 years ago (*2*), at which time it covered an area of about 13×10^6 km^2, similar in dimensions to that of the present-day Antarctic Ice Sheet (*3*). After about 18,000 years ago this last ice sheet began to shrink, reaching approximately 30 percent of its maximum size about 12,000 years ago with considerable areas uncovered in former south and southwest sectors (*3*). Until now the retreat of this ice cap is known almost entirely by radiocarbon dating of materials associated with the glacial retreat across North America (*2, 4–6*). We present a history of the melting of the southern Laurentide Ice Sheet between about 18,000 and 11,000 years ago based on oxygen isotopic analyses of planktonic foraminiferans in the upper parts of three Late Quaternary deep-sea cores (*7*) from the western Gulf of Mexico (Fig. 1), ranging in