

## Drops and Bubbles in Materials Science

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The following applications of drops and bubbles in materials science are reviewed: Formation of extended p-n junctions in semi-conductors by drop migration; mechanisms and morphologies of migrating drops and bubbles in solids; nucleation and corrections to the Volmer-Weber equations; bubble shrinkage in the processing of glass; the formation of glass microshells as laser-fusion targets; and radiation-induced voids in nuclear reactors. These examples show that knowledge of the behavior of drops and bubbles is important in diverse areas of materials processing and properties, and deserves further fundamental study.

Introduction

Semiconducting junctions can be made in complicated shapes by migration of liquid bubbles in a solid semiconductor. Nucleation of solid phases must be controlled in processing solids and regulating their properties; the theory of nucleation was first derived for the formation of droplets in a vapor. Melting of clear and strong glass requires that bubbles be removed from viscous molten glass, and tiny microshells of glass as laser fusion targets are formed by blowing a bubble inside a drop of molten glass. These examples show the importance of drops and bubbles in processing solid materials. Radiation can form bubbles in reactor materials, weakening them. In each of these areas there have been recent advances or controversies, which will be described in this paper. These examples are not intended to provide a comprehensive review of drops and bubbles in Materials Science, but merely a sample of applications and opportunities.

Semiconductor processing and migration of drops

Commercial processes for making p-n junctions in semiconductors by migration of liquid drops, wires, or sheets have been developed by T. R. Anthony and H. E. Cline of General Electric.<sup>1-4</sup> Molten metallic drops or wires move through a solid semiconductor under a thermal or electrical gradient, leaving resolidified doped material in their wake. Drops of a low-melting metal that is a suitable dopant, such as aluminum, are deposited on the surface of the semiconductor, which is then heated and subjected to a temperature gradient or electrical field. In practice there are a number of problems in controlling the shape of the liquid region and its path that require careful control of the temperature and the gradients. Thus knowledge of the morphology and kinetics of the liquid drops and wires is important for successful production of a satisfactory device. Thermal gradients proved to be difficult to control, so electromigration was developed as an alternative.<sup>3</sup>

A lattice of columnar p-n junctions through a semiconductor wafer can be made by thermal migration of aluminum drops through silicon.<sup>5</sup> This "deep-diode array" can be used as an imaging target for x-rays and infrared radiation.

A liquid drop in a gradient of driving force in a solid moves by dissolution and reprecipitation of solid in the liquid. Driving gradients can be in temperature, mechanical force (accelerational field) or electrical potential. Anthony and Cline found that high force gradients were required to migrate brine drops in solid KCl,<sup>5</sup> suggesting that an impractically high sedimentation field would be required to move liquid drops in semiconductors.

The rate of droplet motion can be controlled either by the rate of diffusion of solute in the liquid or by the rate of dissolution of solid (interface control). This dissolution rate is usually proportional to the solubility of the solid in the liquid drop, and can be different for different crystallographic planes in the solid. At high temperatures convective flow in the drop can lead to rates higher than expected from the static diffusion coefficient of solute in the liquid.<sup>7</sup> For large drops diffusion in the liquid is more likely to control the rate of droplet migration, whereas for small drops interface rates become important. A similar influence of crystal size is found for the rate of crystallization from solution. For large crystals diffusion in the liquid controls the rate of growth, whereas for small crystals interface control is usual.<sup>8</sup>

At equilibrium the shape of a liquid drop in a solid is controlled by the interfacial energies of different crystallographic planes of the solid in contact with the liquid. The shape that minimizes the total surface free energy is the equilibrium one. In principle

this shape can be calculated from knowledge of the surface energy as a function of crystallographic orientation of a surface facet by the "Wulff" construction; in practice this function is hardly ever known in much detail, and the relative values of interfacial energies are often deduced from equilibrium shapes of crystals. One would expect that low index and closely-packed crystallographic planes should have the lowest energies, so that these planes should, and usually do, predominate in equilibrium shapes of crystals.

Brine droplets in  $KCl$  had mainly (100) planes as faces after seven years at room temperature, with edge roundings and some contribution from (110) faces.<sup>9</sup> Silicon exposes mainly (111) planes in contact with liquid, with some contribution from (100) planes.<sup>10</sup> When a droplet migrates in a force field, its shape can be distorted by nonuniformities in the field and in the rates of interfacial dissolution.<sup>10</sup>

The rate of migration of gas-filled bubbles in  $KCl$  in a temperature gradient was determined by the rate of evaporation of solid and by diffusion of  $KCl$  molecules in the bubble, in much the way as the liquid drops.<sup>11</sup> The bubbles were bounded by (100) planes, but stretched out in the direction of migration instead of remaining cubic.<sup>12</sup> The shape was determined by the interfacial rates of evaporation and deposition rather than by the equilibrium condition from surface energies. A trail of fine bubbles followed in the wake of the migrating bubble.

### Nucleation

The transformation of one phase into another almost always requires formation of a molecular cluster of the new phase in the old, after which the new phase grows at the expense of the old. This nucleation and growth mechanism is valid for pure materials and usually for mixtures; in some mixtures a uniform transformation called spinodal decomposition is possible, but it will not be considered here. When a cluster or nucleus forms the resultant surface energy can exceed the volume free energy difference driving transformation, so that a nucleation barrier exists even when a large sample of the new phase is stable with respect to the old. This situation is illustrated in Figure 1, where the chemical

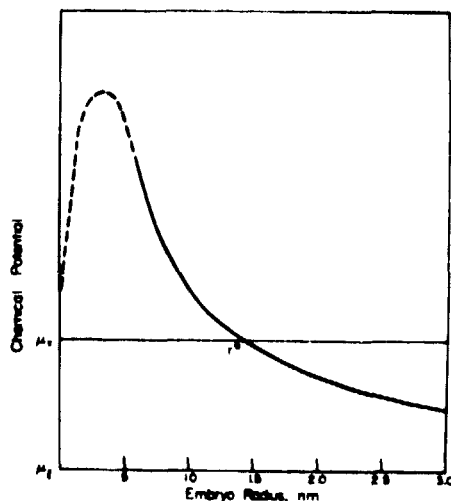


Figure 1. The chemical potential of ethanol drop at  $-9^{\circ}C$ , as a function of drop radius.

potential  $\mu_r$  in  $\text{J/molecules}$  of a drop of ethanol is compared to the chemical potential of supersaturated ethanol vapor  $\mu_v$  and the chemical potential of liquid ethanol  $\mu_l$ , all at  $-9^{\circ}C$ . When the chemical potential of a drop equals that of the surrounding vapor it is said to be of critical size (radius  $r^*$ ). Smaller drops are unstable and decompose; larger drops grow.

Volmer and Weber derived the number of critical nuclei as a function of supersaturation and temperature from the fluctuation theory of Einstein<sup>14</sup> and the calculation of Gibbs<sup>15</sup> of the reversible work to form a sphere of the critical size. The result is

$$N^* = N \exp(-W/kt)$$

(1)

where  $N^*$  is the number of critical nuclei per unit volume,  $N$  is the number of vapor molecules per unit volume,  $W$  is the reversible work to form the critical nucleus,  $k$  is Boltzmann's constant and  $T$  the temperature. Then the rate of nucleation  $I$  is the product of the number of collisions of vapor molecules with the surface of a critical nucleus with  $N^*$ :

$$I = Z A^* N^* \quad (2)$$

where  $Z$  is the collision frequency of molecules with a surface and  $A^*$  is the surface area of a critical nucleus. For a spherical nucleus:

$$W = 16\pi\gamma^3/3(\Delta P)^2 \quad (3)$$

where  $\gamma$  is the surface energy of the liquid and  $\Delta P$  is the difference in pressure between the inside and outside of the critical nucleus.

The equations of Volmer and Weber agreed well with experimental data in rain formation of various liquids in a cloud chamber<sup>16</sup> and with more recent results in the diffusion cloud chamber, especially in the calculated and measured values of the surface energies. Nevertheless a number of authors have suggested that the equations of Volmer and Weber need to be modified by correction factors that vary from a factor of  $10^{17}$  in the nucleation rate to a negligible correction.<sup>17-20</sup> These treatments involve questionable assumptions of equilibrium in chemical deposition reactions to form the critical nucleus or between embryos not of the critical size and the surrounding vapor. The equations of Volmer and Weber agree well with experiment, and there appears to be no need to correct them.

In a recent paper Carlon has found that even undersaturated water vapor and moist air contain multimolecular clusters of water.<sup>21</sup> Thus the initial condition of a vapor in a nucleation experiment may not be just individual molecules, but could contain an unknown distribution of clusters. Such a distribution would further complicate nucleation theories based on a series of condensation reactions, but should not influence the equilibrium fluctuation method of Volmer and Weber. Carlon also found that these clusters of water molecules lead to infrared absorption at wave lengths different from those for molecular water.

#### Bubbles in the processing of glass

Fining, or the removal of bubbles from a glass melt, is one of the major technological problems in glass melting. It is usually solved by holding the glass for some time at a temperature somewhat below the highest melting temperature, and by adding certain minor constituents to the original glass batch. The mechanisms by which these additions aid bubble removal are still somewhat uncertain, although much progress in understanding has been made in recent years.

Bubbles can be removed from a melt by either of two ways. They can rise to the surface or the gas in them can dissolve in the glass. The rate of rise is given by the following equation:

$$\frac{dh}{dt} = \frac{2\sigma g R^2}{9\eta} \quad (4)$$

where  $\sigma$  is the density of the glass,  $g$  is the gravitational constant,  $R$  is the bubble radius, and  $\eta$  is the viscosity of the glass. For a viscosity of 100 P, typical for melting temperatures, the rate of rise of bubbles 0.1 mm in diameter is about 10 cm/day, which is too small to eliminate them from a normal glass furnace. Thus small bubbles can be removed from glass melts only by dissolution of their gas into the glass melt, although larger bubbles can rise to the surface.

Arsenic oxide is a common fining agent added to glass to help remove bubbles. For many years it was thought that the arsenic released oxygen at glass melting temperatures, which "swept out" the bubbles in the glass. However, the calculation above shows that such a mechanism would not eliminate small bubbles, and the elegant experiments of Greene and co-workers showed that arsenic enhances dissolution of oxygen bubbles in glass.<sup>22-24</sup> Thus the importance of arsenic and antimony oxide additions to the glass is to aid in removal of fine bubbles, rather than to generate more gas.

Studies of bubble shrinkage in glass can help in understanding the kinetics of fining, the rates of diffusion of gases in molten glass, and the theoretical treatment of bubble dissolution. Greene and his co-workers observed the shrinkage of oxygen and sulfur dioxide bubbles in a number of silicate glasses between 1000°C and 1300°C.<sup>22-23</sup> They sealed a small amount of gas into a hole between two glass discs, which were then heated in a rotating silica cell. During the first few minutes of heating the temperature of the bubble changed,

so that reliable measurements were not possible. This technique also often introduced a small amount of foreign gas into the bubble. To avoid these difficulties Greene and Davis developed a technique in which the bubble was observed just after it was blown into the molten glass, and studied oxygen, nitrogen, and water bubbles in molten boric oxide.<sup>24</sup> Brown and Doremus<sup>25</sup> also used this technique to study the shrinkage of air oxygen, and nitrogen bubbles in molten boric oxide; an example of their work is shown in Figure 2.

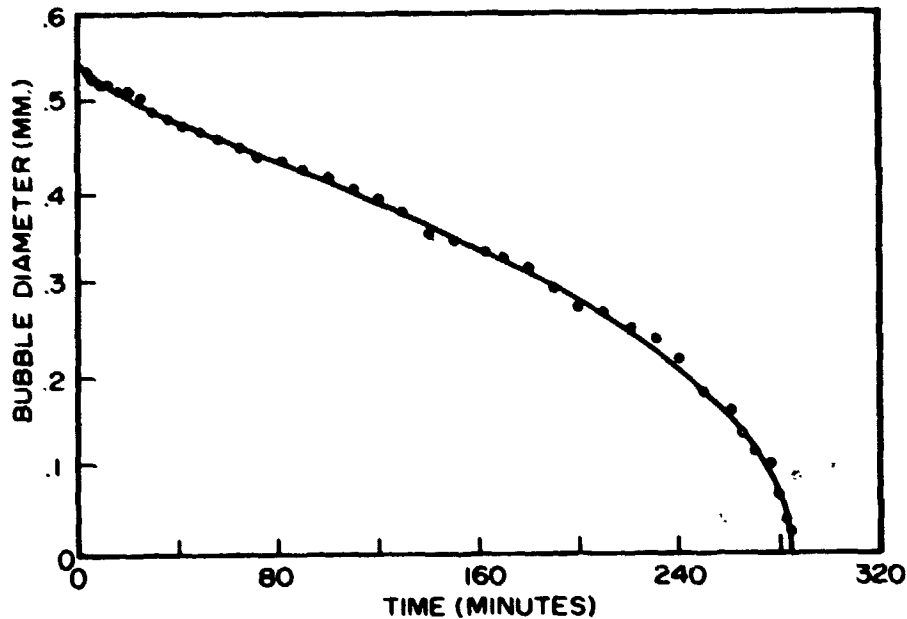


Figure 2. Diameter of an air bubble in molten  $B_2O_3$  at  $550^\circ C$  as a function of time. Circles data; line from eq. 5 with  $D = 2.3(10)^{-7}$   $cm^2/sec$  and  $B = 0.058$ .

The mathematical treatment of the growth or shrinkage of a bubble requires solution of a non-linear partial differential equation, and a general analytical solution has not been found. However, several limiting cases can be solved satisfactorily. If the gas dissolving in the glass has a low concentration (dilute solution in the glass), a relatively simple relation for the radius of the bubble  $R$  as a function of time  $t$  is found:<sup>25,26</sup>

$$R_0^2 - R^2 = 2DBt \left( 1 + \frac{2R_0}{r} \frac{dR}{dt} \right) \quad (5)$$

where  $R_0$  is the initial bubble radius,  $D$  is the diffusion coefficient of the dissolving gas in the glass, and  $B$  is a concentration factor  $B = (c_i - c_\infty)/c_s$ , where the subscripts denote concentrations of gas:  $s$  in the bubble,  $i$  dissolved in the glass at the bubble-glass interface, and  $\infty$  dissolved in the glass far from the bubble. Eq. 5 fits data for the dissolution of air in molten boric oxide as shown in Figure 2.

If the amount of gas dissolved in the glass is not small, ( $B \nless 1$ ), the solution becomes more complicated, because the flow of molten glass as the bubble shrinks leads to a "convection" term in the differential equation.<sup>27</sup> True convection in the glass melt is not significant because of the high viscosity of the glass. A perturbation solution of this expanded differential equation for bubble growth or shrinkage has been given by Duda and Vrentas;<sup>28</sup> the first term in their solution is eq. 5.

Further complications arise if more than one kind of gas is dissolving in the glass,<sup>26,29,30</sup> if the glass sample is not large compared to the bubble,<sup>26</sup> and if there is a surface chemical reaction of the gas dissolving in the glass.<sup>31</sup>

Hollow glass shells filled with deuterium and tritium can serve as laser-fusion targets. These shells are typically about 100  $\mu m$  in diameter with a wall thickness of a few microns, and can be made by dropping powder of a metal-organic gel through a furnace tower at temperatures of from  $1200^\circ C$  to  $1500^\circ C$ .<sup>32</sup> The organic material and residual water serve to blow out the glass into a spherical shell. The size and quality of the shells are dependent on the glass composition, the organic content of the gels, and the furnace conditions.

## Swelling of materials in fast reactors

The swelling of radiation-induced voids in metals and alloys in nuclear reactors can lead to serious degradation of these materials, and may become a problem in fast breeder reactors. The rate of swelling is strongly dependent upon the composition of the irradiated alloy; minor additions ("swelling inhibitors") can reduce the amount of swelling by up to two orders of magnitude.<sup>33</sup> Nucleation of the voids may be a critical step in their formation.<sup>34</sup> Bubbles of gas in irradiated metals can grow by migration and coalescence. The rate of migration of small bubbles is controlled by surface diffusion, and in larger bubbles by ledge nucleation, in niobium alloys and zirconium.<sup>35</sup>

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