

E-BEAM INDUCED DECOMPOSITION OF INORGANIC SOLIDS

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ABSTRACT

A general model for the e-beam induced decomposition of covalent and ionic inorganic solids is outlined. The primary electron beam produces energetic electron/hole pairs; these decay to the band edges, and either recombine or participate in the chemical decomposition of the solid. The kinetics and mechanism of several systems is discussed, including CdCl_2 and PbI_2 . The importance of temperature in decomposition is remarked and it is suggested that induced decomposition mostly starts at 0.6 melting point (K). The usefulness of various inorganic systems, as resists, for x-ray masks, for local indiffusion sources and for metal inter-connects is noted.

1. INTRODUCTION

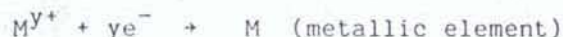
We have, over the last fifteen years, been studying the photon and electron induced decomposition of various inorganic solids (1-11) in thin film form. The purpose of this work has been to measure the kinetics, and deduce the mechanism of the decomposition processes; also to demonstrate the potential usefulness of these decomposition processes in various solid state micro-lithographic procedures.

It is the intention in this paper to present a summary of our work with thin film inorganic materials, noting some of the unifying features of such systems; to compare and contrast some aspects of organic and inorganic systems, and to speculate about various processing applications.

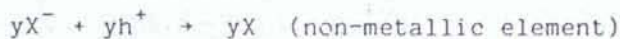
2. FUNDAMENTAL CONCEPTS

Our concern is with polycrystalline thin films ranging in thickness from about 0.04 to 1 μm . These materials are non-metallic, having band gaps from ca. 2 to 8eV, and are variously described as covalent or ionic solids. In all cases the first thing, which is required for decomposition, is the creation of electron/hole pairs by the inducing radiation. Thus for photolysis we need light of energy equal to or greater than the band gap energy. For radiolysis by e-beams, the general tendency is to work with electrons in the 1-50 KeV energy range; the primary, high energy electron, creates a shower of electron/hole pairs along its path, these latter usually have energies about three times that of the band gap (12). The energetic electron/hole pairs created near the peaks in the density of states will rapidly lose energy to the lattice, falling to band gap energy. We are next concerned with the fate of these excess electron/hole pairs which are energetically at the band edges, and spatially distributed throughout the grain in which they were created.

The excess electron/hole pairs may recombine, and/or may participate in the chemical decomposition of the solid. Recombination might occur in the bulk of a grain at various singularities, at the grain boundary, or at the free boundary of the film. Chemical decomposition will occur by reactions such as:



and



for substances like MX_y .

There will be the usual sequence of chemical steps, one being rate determining. The site of the reactions may be in the bulk or at the surface. There may well be a rate determining transport step and the build-up of reaction products will cause vast difficulties in interpretation.

3. EXAMPLES OF INDUCED DECOMPOSITION

The conclusions of a number of studies of induced decomposition are given below, and it is suggested that these may form the beginnings of a useful classification.

3.1 Cadmium Chloride, $CdCl_2$ (7,8). This material is readily evaporated in a vacuum system to give polycrystalline thin films whose mean grain size is about equal to the film thickness. The vapour pressure of $CdCl_2$ is such that at 467K (194°C) the evaporation rate of a deposited film would be 10^{-3} nms^{-1} , while the rate is about hundred times higher at 523K (250°C); this means that $CdCl_2$ can be used as an e-beam resist material up to about 473K (200°C) without serious loss by evaporation. Electron beam irradiation results in the reaction,



(The chlorine atoms mostly combine to desorb as Cl_2 molecules). Above about 363K (90°C) cadmium (as well as the Cl_2) is volatile, so the physical result of e-beam irradiation is progressive thinning of the exposed area. The total removal of reaction products makes mechanistic analysis very considerably easier.

It has been found in all the chemical systems we have studied that the rate of decomposition at fixed flux increases with temperature, typical of an activated process. We have, in addition to temperature, investigated the effect on reaction rate of electron energy, beam current density, film thickness, film doping and mean grain size. A typical decomposition rate curve is shown in Figure 1.

The mechanism proposed for $CdCl_2$ decomposition is: holes are trapped at surface chloride ions which have become special sites because of some local spatial singularity, the chloride ion plus trapped hole moves to a new surface site - this is the rate determining step - from which chlorine either desorbs directly or combines with another (mobile) surface chlorine atom and then desorbs. The cadmium ion, which is made singular by the chloride ion removal, rapidly traps the necessary two electrons and, the system being warm enough, the atom desorbs into the vacuum.

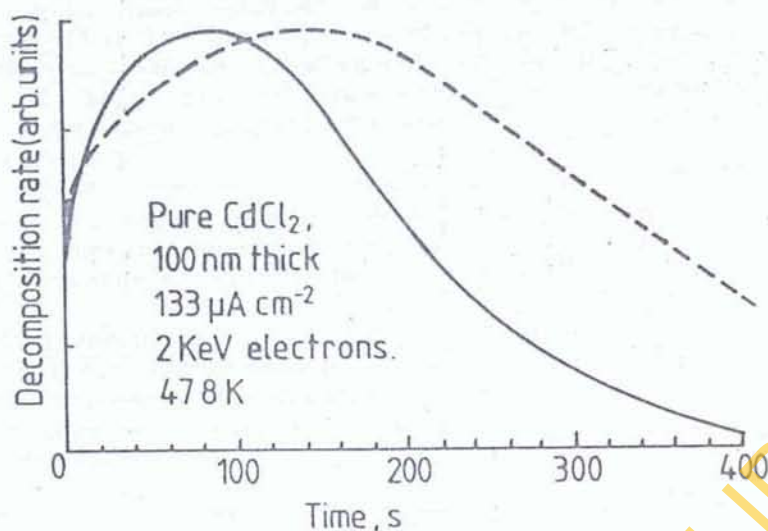


FIGURE 1. Chlorine evolution rate versus time for e-beam irradiated CdCl_2 (PbCl_2 decomposition is shown as the dashed line)

The curve shown in Figure 1 is explained, in a manner consistent with the proposed mechanism, by suggesting that the initial rising portion is a result of increasing the surface concentration of chloride ion singularities as the decomposition of the film progresses. The decaying portion of the curve results from a decreasing concentration of electron/hole pairs per unit area because the film is thinner than the Grun range (see later). Finally the exponential tail must correspond to the film becoming discontinuous. The chlorine evolution rate may be written

$$J = \ell C [1 - p \exp\{(\ell-L)/\ell_0\}]$$

The initial film thickness is L ; the film thickness at any time is ℓ and ℓ_0 is a constant proportional to the initial rate of increase in the density of special surface chloride ion sites. The constant C is proportional to the reaction rate constant and the flux density, and p is related to the factor by which the initial density of special sites increases over the full course of the decomposition.

The above type of decomposition should be classified as, surface decomposition system, with only one solid phase.

Lead chloride (10) and iodide (1-3): Lead is not volatile, so that the decomposition of these lead halides results in the evolution of halogen and the formation of lead clusters throughout the lead halide matrix. Study of the initial stages of photo-decomposition of PbI_2 at low decomposition rates (1) showed that rate was proportional to the area concentration of excess electron/hole pairs. Analysis of all the variables, plus a comparison with the electrical transport properties of the PbI_2 , led to the proposal that the rate limiting step was the transport of negative ion vacancies - generated by halide ion discharge - from the free surface to the interior, where they were annihilated together with positive ion vacancies.

E-beam decomposition kinetics of PbCl_2 (10) is not the same as that for PbI_2 , it is closer in apparent behaviour to CdCl_2 , while retaining some essential differences. The dashed line on Figure 1 is the

normalized (to peak maximum) rate of PbCl_2 (10) decomposition for 2KeV electrons; flux $140 \mu\text{Acm}^{-2}$, film 90 nm thick, temperature 483K (210°C). The mechanism has not been worked out as yet, but it seems that the growth of lead clusters plays a role in reducing the chemical decomposition rate, possibly by decreasing the diffusion length of the excess carriers.

The above decomposition should, for PbI_2 , be classified as: bulk transport, two solid phases, while for $(\text{PbCl}_2/\text{CdCl}_2)$ solid solution it should be surface decomposition: two solid phases, and for PbCl_2 we do not yet know the mechanism, but it is two solid phases.

3.2 Miscellaneous systems. SnI_2 (4-6), Al_3 (9), GaI_3 (9) and AsI_3 (9) all completely photo-decompose, and should readily be decomposed by energetic e-beams. The disadvantage of the tri-iodides of Al, Ga and As are that they are highly volatile (the induced decomposition was carried out at 250K).

4. A ROUGH GUIDE TO STIMULATED DECOMPOSITION

We wish to be able to know under what conditions a solid might be photo- or e-beam decomposed. It is obvious that we need to produce free carriers at the band edges. It is also obvious that we need to make the chemical pathway as favourable as possible as compared with the physical (recombination) pathway. Clearly this can be achieved by increasing the temperature, which has little effect on recombination, but which exponentially increases chemical reaction rates. There would seem to be a correlation between chemical rate and the binding energy of the solid, and it is therefore proposed that there should also be a correlation with melting point, for example approximately 5% usage of electron/hole pairs at $0.6 \times$ melting point (K); this fits our data fairly well.

The absorption of radiation is straightforward with photons, but there is a greater lack of precision where electrons are concerned. A useful guide for electron absorption is to use the Grun range, R , which is defined as the value of x obtained upon extrapolation to zero of the straight line part of the dE/dx vs x curve: dE/dx is the energy loss with distance and x is the distance into the solid. An empirical expression (13) which applies well in the 1 to 50 KeV energy range, in nm, is

$$R = 100E^{1.44}/\rho$$

where ρ is the density of the thin film, in g/cc; and E is the primary electron energy in KeV.

It would seem that mean grain size does not have a noticeable effect upon recombination rate, i.e. internal grain boundaries do not offer efficient recombination centres. However, mean grain size is important in determining resolution when these inorganic materials are used as resists, since the electron/hole pairs produced by the radiation pervade the grain and are not a cloud along the particle track, as might be nearer the case for organic resists. One final point about grain boundaries, is that we take it that electron/hole pairs do not diffuse from grain-to-grain, because the grain boundary is a barrier (double-Schottky) to carrier transport.

5. APPLICATIONS

A partial listing of potential applications is given below, together with some comments.

5.1 Resists: Inorganic resists are significantly different in behaviour and usage from organic resists. They are thin films (~ 50nm thick) and so might well function without need for planarization. Resolution is determined by mean grain size, and is not sensitive to development procedures. Inorganic resists do not suffer significantly from the proximity effects that organic resists have to endure. Since inorganic resists are evaporated, it is possible to deposit over a limited area (using mechanical masking), so making local processing possible. Removal of resist is usually a matter of aqueous solution wash at room temperature.

Organic resists are very much more sensitive than inorganic resists ($5 \mu\text{Ccm}^{-2}$ compared with 2mCcm^{-2}). There are possible inorganic over layer schemes which might be employed in order to improve sensitivity, but these have yet to be tested.

Inorganic resists would appear to be considerably more chemically resistant in reactive ion (or plasma) etching, giving the probability of selectivities of 50 and more.

5.2 Metal masks and patterns: When substances such as PbCl_2 are decomposed the lead left behind tends to be globular in texture. The texture can be made continuous and less globular when a solid solution of $0.8 \text{ PbCl}_2 : 0.2 \text{ CdCl}_2$ is decomposed. Such a system should be useful in the fabrication of X-ray masks for VLSI.

The possibility exists to deposit thin films of metal compound and to decompose these using an e-beam system. Such a procedure might be useful in making metal inter-connects. Thus MoO_3 (m.pt. 1068K) might be a candidate for Mo inter-connects (decomposition temperature estimated to be 640K).

5.3 Local sources: Another possibility inherent in e-beam decomposition of inorganic thin films is the production of local indiffusion sources. Thus e.g., the decomposition of zinc iodide on GaAs to give a local indiffusion zinc source exists. It may, of course, be the case that the local source material is too volatile at the indiffusion temperature, in which case it would be necessary to coat the sources in a chemically inert, removable, low-volatility material.

6. CONCLUSIONS

The e-beam decomposition of semiconductors and insulators follows along much the same lines as photolysis, namely the production of electron/hole pairs by the stimulating radiation followed by the use of a fraction of these excess carriers in the decomposition process.

E-beam stimulated decomposition of various inorganic solids can be used in a variety of solid state fabrication processes.

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