Electron beam decomposition of $CdCl_2$

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The *e*-beam stimulated reaction, $CdCl_2$ (s)→Cd(s) + 2 Cl(g), has been studied in cadmium chloride thin films between 303 and 483 K using 2-keV electrons. The dose required to make 90-nm-deep holes at 483 K is 3×10^{-3} C cm^{-2}. Extrapolated dosing levels of $\sim6\times10^{-5}$ C cm^{-2} are expected. The use of $CdCl_2$ as a positive-type electron resist in a new scheme is proposed. A working model, useful for considering the *e*-beam stimulated decomposition energetics and mechanism, is briefly discussed.

In this communication we report on the electron beam (*e*-beam) decomposition of thin films of cadmium chloride, $CdCl_2$, and suggest that it might have potential as a resist in a new lithographic scheme: compare other inorganic resists.[1-3] In addition, we suggest a rough, but useful, model for considering *e*-beam stimulated decompositions of inorganic solids based on our experience of photolysis.

The reason for choosing to investigate $CdCl_2$ is based upon our notions for the possible lithographic scheme shown in Fig. 1, and for this reason we give an outline description of the hypothetical scheme. Step (a) is the vacuum deposition of thin film (~100 nm) of $CdCl_2$. The resist is chosen so that, among other things, its *e*-beam decomposition products are volatile at the irradiation temperature and the resist can be reevaporated (as shown in the last step): Fig. 2 shows the relevant vapor pressure curves.[4] The second step is exposure to the *e*-beam in selected areas at an elevated temperature. The electrons cause the resist chemically to decompose (this process, when particle initiated, is called radiolysis) and the volatile products are cadmium and chlorine. The $CdCl_2$ can, in this way, be completely removed exposing the underlying layer, or, much more likely, the $CdCl_2$ can be partially removed and then the entire resist layer uniformly thinned down until the underlying surface is exposed in the selected areas. The dry etching step is selected to be compatible with the resist. Thus $CdCl_2$ will certainly be compatible with a chlorine radical containing plasma and it will most likely be compatible with fluorine-based plasma. The fourth and last step is to raise the substrate temperature to a value where reevaporation of $CdCl_2$ is rapid; cf. Fig. 2. Thus we see that this is a scheme for an *inorganic, e-beam, plasma-compatible, volatile resist*, and it should reduce the number of handling operations considerably.

We report here our preliminary work on the electron radiolysis of $CdCl_2$. Anhydrous $CdCl_2$ [B. D. H. Chemicals Ltd. (U. K.)] was thermally evaporated from a molybdenum boat onto silicon substrates at room temperature. A shuttered evaporation system was used: the $CdCl_2$ evaporation rate was brought to the steady value of 3 nm/s and the shutter then opened for the necessary time.

The $CdCl_2$ films, examined in the scanning electron microscope, were seen to have a polycrystalline structure, with

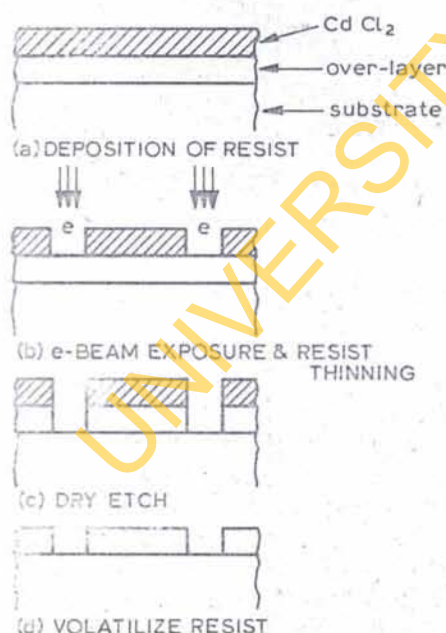

FIG. 1. Proposed lithographic process.

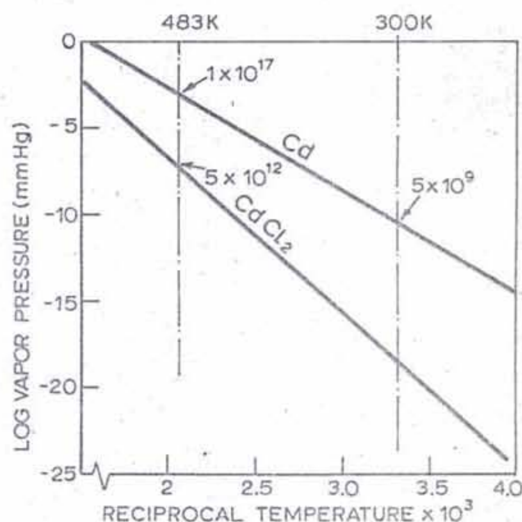

FIG. 2. Vapor pressure of $CdCl_2$ and Cd. Evaporation rates, calculated assuming unity sticking coefficient, are shown at various parts of the curves as number of particles cm^{-2} s^{-1}.

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mean grain size about equal to the film thickness. The specimens, mounted on a heated platform, were placed on a manipulator in an ultra-high vacuum system, base pressure $\sim 7\times 10^{-9}$ Torr. The electron beam used, taken as Gaussian-shaped, had an effective diameter of 300 μm (i.e., 2% edge-to-center intensity ratio) and beam energy of 2000 eV (V. G. Ltd., LEG 22 *e*-gun and power supply). The beam current was measured using a Faraday cup. The $CdCl_2$ film, of known thickness, was irradiated for a known time, current density, and substrate temperature; the specimen was then moved, while still in the vacuum, and a different area irradiated. The specimen was finally removed from the vacuum. The area of each spot was measured under the microscope. The depth and profile of each hole was measured by scanning with a stylus depth-measuring instrument [Talystep, Rank, Taylor Hobson Ltd. (U. K.)] and the composition inside and outside the resist hole was measured by means of electron probe x-ray analysis. The volume of material removed by decomposition was determined from the above measurements, fitted to a Gaussian, and was found to be linear in dose over the range 10^{-5}–3×10^{-3} C/cm^2.

Our results show that the holes produced in the resist for all the conditions used in this study were a result of radiolysis and not thermally induced. These results are also in accord with the temperature profile study of Iranmanesh and Pease.[5] For irradiation at 30 and 60 °C, x-ray studies showed that cadmium remained behind. Irradiation at higher temperatures resulted in completely volatile products. The "efficiency" of the radiolysis process was measured for holes about 90 nm in maximum depth (in a 140-nm-thick $CdCl_2$ film). The efficiency, in moles per coulomb, as a function of temperature, is shown in Fig. 3. The energy employed

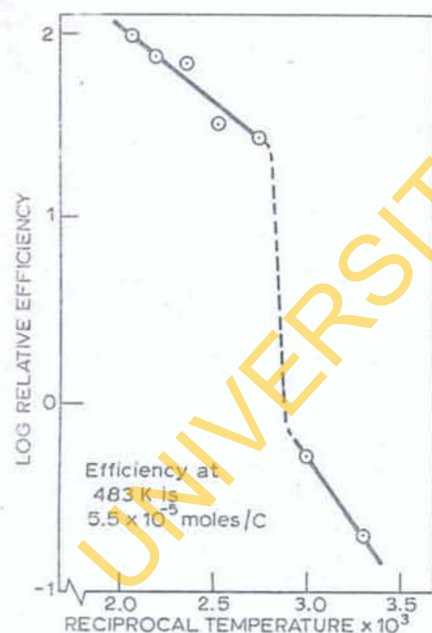

FIG. 3. Efficiency for the *e*-beam decomposition of $CdCl_2$ on silicon as a function of temperature, using 2-keV electrons.

using 2 keV electrons was 2000 ÷ efficiency, i.e., 3.6×10^7 J/mol at 483 K. This required beam energy may be compared with the standard heat of the reaction, $CdCl_2$(solid)→Cd (solid) + 2 Cl (gas), which is 6.3×10^5 J/mol, giving a 1.8% "thermodynamic" efficiency. Or if, instead, we compare the energy used with the energy to form 2 mol of hole/electron pairs at the band edge, which is estimated to be $\sim 9\times 10^5$ J/mol (of $CdCl_2$) we obtain an "electronic" efficiency for 2-keV electrons at 483 K of about 2.5%. The requirement for a 90-nm depth hole is $\sim 3\times 10^{-3}$ C/cm^2.

The usefulness of $CdCl_2$, and similar materials, as an electron resist in some lithographic schemes will depend on a number of considerations, one of them being the charge per unit area requirement. We have obtained 3×10^{-3} C/cm^2 but we are certain that this can be improved, and we argue along the following lines. We take it that we start with a 100-nm-thick $CdCl_2$ film. A Grün electron range[6] in such a film would correspond to 4-keV electrons, so we could obtain a twofold improvement by increasing our beam voltage. We do not have to remove all the $CdCl_2$ under the beam. Thus if we cut features to a depth of 30 nm and then thin the 100-nm film by 70 nm we should produce our windows for one-third of the previous energy requirement; a threefold improvement. Finally there is the possibility of improvement in the decomposition sensitivity of the $CdCl_2$ itself. The hole/electron pairs at the band edge (see later for mechanistic discussion) can either recombine or partake in the $CdCl_2$ decomposition. Doping the $CdCl_2$ with monovalent chlorides such as CuCl and AgCl (which increases the chlorine vacancy density) will increase the relative usage of hole/electron pairs for decomposition, as has been shown in various photolysis studies.[7,8] We can only make a rough guess as to what this improved efficiency might be. Thus suppose that about one-third of the primary electron energy eventually appears as band-edge hole/electron pairs (energy gap ÷ energy from center of valence band to center of conduction band, $\approx 1/3$ then our overall 2.5% "electronic" efficiency really becomes 7.5% efficient use of hole/electron pairs at the band edge (the other 92.5% recombine). Doping might be expected to raise the 7.5% to about 60%, i.e., a factor of 8. Thus the final dosage required might be about $(3\times 10^{-3}$ C/mol)/$(2\times 3\times 8)\sim 6\times 10^{-5}$ C/mol.

Clearly, resolution is another important matter. We do not expect the spread of generated hole/electron pairs beyond the thickness of a grain since it is at grain boundaries that recombination is generally supposed to take place. The grain size for room-temperature-deposited $CdCl_2$ is about equal to the grain thickness, namely 100 nm, so we expect resolution to be about 100 nm.

An approach useful in contemplating the electron radiolysis of inorganic materials is to divide the overall process into two parts. First, we are concerned with primary electrons creating a shower of electron/hole pairs, which, of course, has a complicated energy distribution. A substantial fraction, one-third (?), must appear as electron/hole pairs at the conduction and valence-band edges of the resist material. And now the fate of these electron/hole pairs is our next concern. They can either recombine (at the surface or in the bulk) or they can take part in the chemical decomposition of

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the resist. At this stage the kinetics and mechanism follow closely what occurs in photolysis. Thus if one can photolyze a substance, we would say it should decompose under the electron beam. Photolysis of substances such as PbI_2[7] and α-SnI_2[8] are thermally activated with an energy of 0.45 and 0.29 eV, respectively, and we therefore expected, and found, the radiolysis of $CdCl_2$ to be likewise activated.

We intend to extend the range of our study of $CdCl_2$ resist and to examine HgF_2 and CsF as potentially useful material, especially for x-ray masks. Furthermore, we expect that a further improvement in efficiency (i.e., doses of $< 10^{-5}$ C cm^{-2}) can be achieved by employing various surface-sensitive schemes, for example, as used with PbI_2.[9]

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