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Letter

Cadmium chloride thin films: hydration–dehydration

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We have been using polycrystalline thin films of anhydrous cadmium chloride ($CdCl_2$) as an electron beam positive resist for the fabrication of features in SiO_2-coated silicon wafers[1]. The kinetics and mechanism of the electron-beam-induced decomposition of $CdCl_2$, which is the resist reaction, have been studied in detail[2]; this work required that we know the thickness, and density, of the film. In the ordinary way of things, film thickness and density determination is a routine matter, but $CdCl_2$ films hydrate on exposure to the laboratory atmosphere, becoming $CdCl_2 \cdot xH_2O$, with a corresponding change in density and thickness. It was therefore necessary to undertake the study, which is reported here, of the hydration–dehydration of $CdCl_2$ thin films.

Anhydrous cadmium chloride, of purity 95%, in the form of a fine powder, was used as source material (BDH plc). This material was evaporated in a conventional 18 in diameter "bell-jar" system (pressure about 10^{-6} Torr, with a liquid nitrogen trap). The cadmium chloride was loaded onto a dimple-type molybdenum resistive strip heater boat and heated first to outgas the $CdCl_2$ and then at higher temperatures (about 450 °C) so as to give a deposition rate of about 2000 Å min^{-1} at 20 cm from the source. There was a shutter arrangement so that only steady state, mid-fraction, vapour was allowed to deposit onto the substrate which was either clean outgassed glass microscope slides or clean silicon wafers coated in oxide of known thickness and refractive index.

The excessive low temperature outgassing of the cadmium chloride source material was attributed to the decomposition of a $CdCl_2 \cdot H_2O$: this is a material with an orthorhombic system of space group *Pnam*, with four molecules in the unit cell of dimensions[3] $a_0 = 9.261$ Å, $b_0 = 11.730$ Å and $c_0 = 3.794$ Å. The X-ray thin film diffraction pattern was obtained using the technique of Wallace and Ward[4].

Hydration–dehydration measurements were carried out as follows. Thoroughly vacuum-outgassed $CdCl_2$ was deposited through a metal aperture onto a calibrated quartz electrode plate of a quartz thickness monitor (QCM). This gave the mass of a known film area in terms of a frequency shift. The thin film was then exposed to the room air: the frequency shifted further, indicating a mass increase (water take-up). The equilibrium values of the frequency shift, corrected for atmospheric buoyancy effects (36 Hz), were noted and are given in the inset to Fig. 1.

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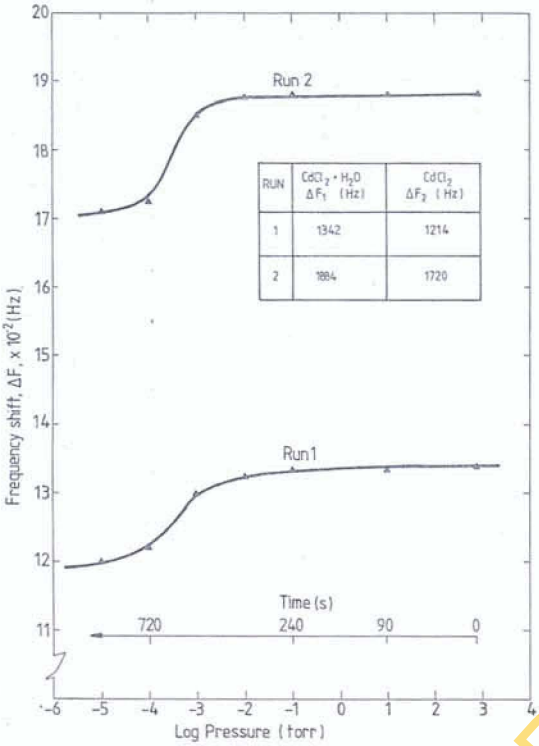

Fig. 1. Weight loss *vs.* total chamber pressure, for hydrated cadmium chloride films. The time origin corresponds to atmospheric pressure and when pumping down of the chamber started. The scale is neither a logarithmic scale nor a linear scale, but with discrete values at specified pressure points.

The reverse process was then carried out, i.e. the film was placed under vacuum: the QCM results are shown in Fig. 1, where it is quite obvious that it is entirely reversible at room temperature. The value of x was calculated for the two runs shown in the inset to Fig. 1. Thus

$$x = \left(\frac{\Delta F_1}{\Delta F_2} - 1\right)\frac{183.5}{18}$$

and we obtained an average value of 1.02, which is entirely consistent with the notion of $CdCl_2 \cdot H_2O$ as the compound formed upon hydration. It is interesting to note the speed and reversibility of this process (the mean grain size in the films was about 1000 Å).

The density of $CdCl_2 \cdot H_2O$ thin film was determined by measuring the thickness of a thin film of known mass per unit area. Thickness was measured by means of a capacitative profilometer (Talysurf, from Taylor Hobson Ltd.) and agreed with optical measurements (ellipsometry). The density so determined was $3.56 \pm 0.14\ g\ cm^{-3}$, the error arising largely from the thickness determinations. The X-ray density of $CdCl_2 \cdot H_2O$ is $3.24\ g\ cm^{-3}$. The difference in density is taken to arise from the fact that the area of the film is constrained to remain constant by the

$CdCl_2$ binding to the substrate: the film must therefore be under considerable compressive stress. Calculating the thickness of a dehydrated film from the known density, 4.04 g cm^{-3}, gives the ratio of thicknesses of $CdCl_2$ to $CdCl_2 \cdot H_2O$ as 0.80.

We report here the refractive index n of $CdCl_2 \cdot H_2O$ at 6328 Å which is not, as far as we know, listed. The value for n is 1.68 ± 0.005.

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3 *Powder Diffraction File*, Joint Committee on Powder Diffraction Standards, Swarthmore, PA, 1977, File 27-23.
4 C. A. Wallace and R. C. C. Ward, *J. Appl. Crystallogr.*, *8* (1975) 255.