

Thin Film Densities*

J. Edgecumbe

Stanford Linear Accelerator Center

Stanford University, Stanford, California

The ease with which film thickness can be determined and controlled with quartz crystal monitors^{1,2} has made such devices widely used in thin film work. The quartz crystal monitor is a very accurate and sensitive means of determining film thickness in g/cm^2 , a particularly meaningful measure of film thickness when studying, for example, electron range-energy relations.³ Unfortunately, in a wide variety of thin film work, it is important to know the film thickness in \AA . Conversion between the two methods of measuring thickness requires knowledge of the density of the deposit. Contradictory data on thin film densities exists in the literature. Thermally evaporated Cu,^{4,5} Ag,^{4,6} Au,⁶ In⁷ and Ni-Fe⁸ were found to have densities below the bulk density by as much as 30%. Recently, Wolter⁹ (Al, Au, Ag, Cu and Cr) and Hartman¹⁰ (Al, Au and Ag) reported densities within a few percent of bulk density for films prepared under essentially the same evaporation conditions as the above films. A possible explanation of these differences has been suggested by Aisenberg¹¹ as due to unequal sticking coefficients when different substrates are used for mass per unit area determination and thickness determination. Another possible source of disagreement is the use of indirect methods to determine the thickness or mass per unit area of samples.

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The data reported below, using direct methods of measurement, was obtained during a calibration of a quartz crystal monitor and is in agreement with the data of Wolter and Hartman in that films of Al, Au, KCl and CsI were found to have densities within a few percent of bulk density.

Thin films of Al, Au, KCl and CsI were prepared by thermal evaporation in a diffusion pumped, freon-refrigerator-baffled bell jar system at pressures ranging from 2×10^{-7} to 10^{-5} Torr. Al and Au were evaporated from spiral W filaments; KCl and CsI from Ta and Mo "dimple" boats, respectively. A source-to-substrate spacing of 6 in. was used and evaporation rates were varied from 8 to 230 Å/sec. No correlation between evaporation pressure or evaporation rate and film density was observed over the ranges given. The substrates used were standard 1" x 3" microscope slides cleaned ultrasonically in Electro-Sol (inorganic soap), distilled water and ethanol. The substrate temperature was not controlled or determined and was probably near room temperature. All evaporants were melted with the substrate shielded by a shutter prior to beginning deposition. The substrates were masked so that the exposed area was 5.92 cm^2 , and the deposition was carried out at normal incidence.

The thickness of the samples, τ' , in $\mu\text{g}/\text{cm}^2$, was determined by weighing the substrates on a Mettler microbalance before and after evaporation. Since the films had to be removed from the vacuum system for weighings, the accuracy was $\sim \pm 6 \mu\text{g}/\text{cm}^2$, limited mainly by handling, dust, and changes in temperature (which produce large changes in apparent weight of a sample on a microbalance). This data was used

to calibrate the frequency change of the quartz crystal monitor. In order to determine the density of the deposit, the films were overlaid with Al or Ag and the geometrical thickness, τ , was determined by multiple beam interferometry. The accuracy of these measurements was $\sim \pm 30 \text{ \AA}$, neglecting the possible existence of a systematic error due to differences in sticking coefficients for the deposit and substrate.¹¹

The density of the film is indicated in Fig. 1 where τ' vs τ is plotted. The solid lines are drawn assuming the bulk density. The average density of all the Au films prepared was $(98 \pm 4)\%$ of the bulk density; for Al the average was $(99 \pm 5)\%$ (where \pm is the standard deviation of the measured values). This data indicates that, to within the accuracy of the measurements ($\sim \pm 5\%$), films of Au and Al have the bulk density for $\tau \gtrsim 140 \text{ \AA}$ and $\gtrsim 525 \text{ \AA}$, respectively. For both KCl and CsI, the results are somewhat different in that the data is displaced a constant amount ($\sim 4 \mu\text{g}/\text{cm}^2$) above the bulk density line. This displacement appears to be due to the hygroscopic nature of these materials. For, after venting the bell jar to dry nitrogen with no effect on τ' , a change in the quartz crystal monitor frequency, corresponding to an increase in τ' by $\sim 4 \mu\text{g}/\text{cm}^2$, was observed when the bell jar was removed, exposing the sample to the atmosphere. The time required to saturate the adsorption process was drastically different for the two materials. Saturation occurred after ~ 10 sec exposure for KCl but required ~ 2 h for CsI. The water vapor appears to be physically adsorbed to

the film for, if the sample is re-evacuated, the monitor frequency returns to the value obtained immediately after deposition, indicating that the water vapor is removed, thus contributing no possible systematic error to the interferometric measurements. The above results indicate that thin films of Au, Al, KCl and CsI have densities within a few percent of the bulk density.

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Figure Caption

Fig. 1. Mass per unit area vs film thickness for evaporated films of Au, Al, KCl and CsI. The solid lines are drawn assuming the bulk density. Dashed lines are the best fit to the data for the alkali halides.

