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SOME OPTICAL PROPERTIES OF VAPOR-DEPOSITED FILMS OF ARSENIC, ANTIMONY, AND BISMUTH

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In the course of a study of vapor deposition of metal films it was noted that above a certain pressure the film deposited on a glass slide did not display specular reflection, but instead displayed a strong absorption of reflected light. These films had black velvety appearance.

It was attempted in this study to determine whether the production of the specularly reflecting and absorbing surfaces of films is a function of the gas pressure, and whether it can be correlated with certain physical and chemical properties of the film-forming metal.

A vacuum evaporation unit consisting of a (Central Scientific) megavac pump and a Distillation Products two-stage diffusion pump, type VWF 30-06, was used. An all-metal vacuum line led from the diffusion pump to a pump plate 18 inches in diameter and bell-jar (Central Scientific). The pump plate was equipped with four electrode connections (stand-off terminals), two of which were used to hold the tungsten filaments for the evaporation of the metals. The vacuum was measured with a Todd-McLeod gauge, which permits the measurement of vacuum between the pressures of 25 cm to 0.00005 mm mercury in three steps.

Chemically pure arsenic, antimony, and bismuth metals in pellets were placed in "baskets." The "baskets" were made by winding soft tungsten wire 0.4 mm in diameter around the conical part of a pencil and compressing the helix thus obtained until the individual windings were not more than 0.5 mm apart. This "basket" was connected with the stand-off terminals of the pump plate. Into this "basket" a few decigrams of the metals mentioned above were placed.

A glass slide (microscope pyrex glass slide) was placed in the bell-jar under an angle of 45°, 15 cm from the "basket." The slide was cleaned with potassium bichromate-sulphuric acid cleaning fluid, rinsed with distilled water, and dried in a vacuum drying oven at 105°C.

After covering the pump plate with the bell-jar, properly sealed with high vacuum silicone grease (Dow-Corning), the fore-pump (megavac) was switched on. After a vacuum of about 50μ was reached, the diffusion pump (silicone oil) was turned on. The replacement of air by helium, being an inert gas, was considered important to prevent chemical reactions of the metal, especially in vapor form at elevated temperatures with the constituents of air. Therefore, when the vacuum of 0.1μ was reached, helium was admitted into the vacuum system to the pressure of 100μ and again evacuated to 0.1μ. This "flushing" process was repeated four times, and after the ultimate vacuum of 0.05μ was reached, helium was admitted to the desired pressures. This process was repeated whenever the vacuum was broken.

After the desired vacuum was obtained, the tungsten filament ("basket") was heated electrically by using a variac-low voltage transformer combination to temperatures measured with an optical pyrometer. The vacuum was checked continually during the evaporation process with a Pirani gauge, and was spot-checked with the McLeod gauge.

In the preliminary measurements, the temperature of the "basket" within 800° to 1,500°C displayed no significant change of the optical appearance of the films, regardless of the metals used for the film deposition. However, at the lower temperature the film formation took more time to develop. Therefore, the measurements were conducted at the "basket" temperature of 1,000°C.

When arsenic was used as film material the transition from specular reflection to absorption of visible light was observed at a helium pressure of 298μ. A lowering of the pressure to 294μ produced specularly reflecting films in all the 20 trials performed, while a pressure of 305μ produced absorbing films in about 20 trials. At a gas pressure of 300μ, 19 or 20 trials showed absorption films. This transition pressure did not change when the "basket" temperature was varied.

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When antimony was used, the transition pressure from specular reflection to absorption was 95μ. Exclusively absorbing films (in all of the 20 trials) were showed at 3μ above, and 2μ below showed specularly reflecting films exclusively (20 trials). When the "basket" temperature was changed, no significant change of the transition pressure was observed.

When bismuth was used the transition pressure between specular reflection and absorption was observed to be 150μ. At 4μ above, and at 5μ below, 100 per cent absorption and specular reflection were shown respectively, in all 20 trials for each pressure quoted.

This indicates that at a well-defined gas pressure the transition from a specularly reflecting to an absorbing film occurs which is specific for the film-forming metal.

The transition pressures mentioned above for all the three metals were determined by interpolation from reflectivity measurements of the films obtained at lower and higher pressures. The method employed can be described as follows:

The reflectivities of films deposited at low pressure (specular reflection film) and high pressure (absorbing film) were determined photo-electrically. The films produced at low pressures (just less than the transition pressure) showed reflectivities of more than 80 per cent of the incident light. Films produced just above the transition pressure showed low reflectivity (between 5 and 12 per cent of the incident light). The transition pressures were calculated by taking the 50 per cent average of the differences of the reflectivities of the absorbing and reflecting films. Since the pressures at which specularly reflecting films and absorbing films were obtained are very close together (only a few μ pressure difference) this interpolation to determine the transition pressure seems permissible. (See Table I).

There seems to be a correlation between the atomic weight, as well as atomic number, and the transition pressure of the metal, although arsenic displays a high transition pressure (298μ). From similar measurements of transition pressures of other elements (Cu, Ag, Al), one can surmise that the higher the atomic number of the element, the higher is the transition pressure.

It would be interesting to continue this study by determining the transition pressures not only of the metals and their alloys, but of non-metals with the goal to verify the correlation suggested above.

Table I. The Transition Pressures, Specific Heat, Boiling Point, Melting Point, Density, Atomic Weight and Atomic Number of Metals Investigated.

	1	2	3	4	5	6	7	8	9
	Atomic number	Atomic weight	Density	Pressure for specific reflection (μ)	Pressure of transition (μ)	Pressure for absorbing film (μ)	Melting point °C	Boiling point °C	Specific heat at 100°C
As	33	74.91	5.727	290	298	305	814(38 at.)	615	0.0822
Sb	51	121.76	6.684	91	95	98	630	1380	.0515
Bi	83	209.	9.8	145	150	154	271	1470	.034