

A SINGLE-SOURCE TECHNIQUE
FOR VACUUM DEPOSITION OF ALLOY FILMS

by

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INTRODUCTION

In preparing alloy films by vacuum evaporation, great difficulty is experienced in controlling the composition of the film. This arises from the different vapor pressures of the constituents. In the case of indium antimonide, for example, at 1200°C, the vapor pressure of Sb in equilibrium with the stoichiometric liquid compound is about one hundred times greater than that of In. Consequently, Sb is evaporated at a faster rate than In during the evaporation; this affects the composition of the vapor, so that the film is of composition different from that of the starting material. If all of the starting material is used up in the evaporation, the film will be stratified, consisting of a layer of Sb overlaid with In-Sb alloy, and finally almost pure In on the surface. Various techniques for producing stoichiometric, non-stratified thin films of InSb by vacuum evaporation have been attempted, and while some of these are promising in principle, none has proved to be experimentally feasible. The method suggested in the present thesis is both theoretically and practically workable, and it is applicable to the vacuum deposition of any binary or multi-component mixture.

REVIEW OF PREVIOUS WAYS OF PREPARING NEAR-STOICHIOMETRIC AND NON-STRATIFIED THIN FILMS OF InSb BY VACUUM EVAPORATION

Techniques which have been used to deposit films of InSb (and other compounds and alloys) in a vacuum can be divided into two categories according to the number of vapor sources being used, namely, single source and two sources.

SINGLE SOURCE

(1) Finely powdered InSb is supplied continuously by a mechanical device such as a moving belt, to heated surface, from which it evaporates as it is supplied.

This method has the disadvantage that the vapor is not of uniform composition and that there is no way to reduce the rate of evaporation of a given particle. Also, there is danger of "spattering" of partially evaporated particles from the boat, resulting in a deficiency of the less volatile component. Finally there is danger of introducing impurities in the process of grinding the charge to powder.

(2) A whole piece of InSb is evaporated in one evaporation and the film is annealed after the evaporation.

The films obtained by this method have layers owing to the changing constitution of the melt, hence of the vapor. Although the effect of annealing causes recombination between In and Sb atoms, it is by no means certain that this recombination is complete. Moreover, the addition of another step (annealing) to the process is not particularly desirable.

TWO SOURCES

Separate crucibles are used for In and Sb. The temperatures are adjusted to vaporize In and Sb at the same rate.

This method should work in principle, but in practice, it is difficult to control the composition within the required accuracy. This is particularly true for semiconducting compounds, such as InSb, where the amount of the two components must be equal within perhaps one part in 10^6 .

THE SINGLE-SOURCE METHOD

DESCRIPTION

The method to be described here is essentially a single-source type evaporation. The vapor source is composed of three parts: crucible, crucible heater, and boat. Material to be evaporated is sealed in the crucible, and it is kept in liquid form by the crucible heater. The melt in turn is led to the boat by a capillary and is evaporated there. One type of vapor source can be specified as the following:

(A) Crucible

The crucible is made of a material, such as tantalum or molybdenum, that is wetted by the melt. The top of the crucible is sealed by a screwed-on lid and the bottom terminates in a capillary leading to the high temperature surface from which evaporation takes place.

(B) Crucible heater

Ideally, a heat shielded type crucible heater should be used to provide uniform temperature throughout the crucible, including the capillary part up to the opening.

(C) Boat

An isolated-hot-zone boat is suitable. The boat is situated just beneath the opening of the crucible. The crucible can be protected from the radiation from the hot boat, by putting a radiation shield between them.

The temperatures of the crucible and boat can be adjusted separately. The boat temperature can be adjusted to a suitable temperature for evaporation. The rate of evaporation can be controlled by adjusting the temperature of the crucible, since the rate at which the melt runs out through the capillary is

determined by the vapor pressure inside the crucible. The temperature of the boat is independently adjusted to a temperature sufficiently high that the steady-state volume of the evaporant in the boat is much smaller than the volume of the crucible.

The following section will show that the constitution of the vapor thus obtained is exactly stoichiometric to the charge inside the crucible.

THEORY

The method under discussion is similar to the first method ("flash evaporation" of powder) mentioned above, in that the feed to the boat is continuous. A very small stream of melted InSb runs out continuously and uniformly from the opening and is completely evaporated from the hot region just beneath the opening. Strictly speaking, however, the liquid is not flash evaporated when it reaches the boat, but rather reaches a steady-state volume such that the rate of evaporation is equal to the feed rate from the crucible.

The evaporation rates E_{In} and E_{Sb} of the two components In and Sb respectively, are related by the expression

$$\frac{E_{In}}{E_{Sb}} = \frac{W_{In}}{W_{Sb}} \frac{P_{In}}{P_{Sb}} \left(\frac{M_{Sb}}{M_{In}} \right)^{3/2}$$

Where W 's are atomic concentrations; P 's, partial vapor pressures; M 's molecular weights. In the low evaporation temperature range from 1000°C to 1200°C, P_{In} is 10^{-1} to 1mm Hg; while P_{Sb} is 10 to 10^2 mm Hg. $M_{In} = 114.82$, $M_{Sb} = 121.76$. Since the initial condition is $W_{In} = W_{Sb} = 50\%$, E_{Sb} is about a hundred times greater than E_{In} . The much faster evaporation rate of Sb causes the mixture on the evaporating surface to become increasingly In rich; hence W_{In} increases and W_{Sb} correspondingly decreases at the surface. But since the furnished melt

is always stoichiometric InSb, a steady state will eventually be reached such that $E_{\text{In}} = E_{\text{Sb}} = 1$. The rate of approach to steady state depends on the volume on the evaporation surface and the rate of flow through the capillary. Denote the concentrations of In and Sb by n_1 and n_2 atoms/cm³, with initial values n_{10} and n_{20} respectively. The evaporation rates are $n_1 P_{\text{In}}$ and $n_2 P_{\text{Sb}}$. The ratio of P's is constant at constant temperature, hence we can write

$$P_{\text{In}} / P_{\text{Sb}} = n_{10} n_{2s} / n_{20} n_{1s}$$

where $n_{10} + n_{20} = n$, and n_{1s} and n_{2s} are two constants. Since only one constant is required to define the ratio $P_{\text{In}}/P_{\text{Sb}}$ we are liberty to choose $n_{1s} + n_{2s} = n$. Then it can be shown (1) that

$$(n_1 - n_{1s}) \exp\left(-\frac{(n_{10} - n_{1s})(n_{10} - n_1)}{n_{1s} n_{2s}}\right) = (n_{10} - n_{1s}) \exp\left(-\frac{n_{10} n_{20} vAt}{n_{1s} n_{2s} V}\right)$$

$$(n_2 - n_{2s}) \exp\left(-\frac{(n_{20} - n_{2s})(n_{20} - n_2)}{n_{2s} n_{1s}}\right) = (n_{20} - n_{2s}) \exp\left(-\frac{n_{20} n_{10} vAt}{n_{2s} n_{1s} V}\right)$$

where V is the volume of the evaporation surface, v is the linear flow rate through the capillary, and A is the cross-sectional area of the capillary. Thus, it is seen that n_1 and n_2 approach the constant values n_{1s} and n_{2s} as time t approaches infinity, and we have

$$n_{1s} P_{\text{In}} / n_{2s} P_{\text{Sb}} = n_{10} / n_{20} = 1$$

as the ratio of the steady state evaporation rates as expected. The rate of approach to this steady state is an exponential function of vAt/V , namely, of the ratio of the total volume evaporated to the volume on the evaporation surface.

(1) E. B. Dale and A. T. Chai,

Two effects that might effect the stoichiometry of the feed to the boat or of the evaporant must be considered, namely, the effect of evaporation within the crucible, and the effect of diffusion from the boat back into the crucible.

Since the top is sealed, no vapor is lost except by evaporation from the boat at the end of the capillary. Thus the constitution of the melt can be disturbed only by possible non-stoichiometric condensation inside the crucible. This does not happen, however, if the temperature of the crucible is uniform, because the composition of each phase in a closed system is constant at thermal equilibrium.

As the concentration of In builds up on the evaporating surface, In begins to diffuse back through the capillary toward the reservoir, and Sb begins to diffuse from the reservoir toward the evaporating surface. This diffusion flow is superimposed on the forced flow through the capillary and, if important, would prevent the establishment of a steady state condition. Let us consider a concentrated layer with constant concentration at the end of the opening of the capillary. This is essentially a problem of forced diffusion from a constant source into a semi-infinite body. The constant flow v of the melt in the capillary can be considered as a drift velocity externally imposed on the diffusing In atoms, which diffuse from the region of high In concentration (namely, the evaporating surface) into the medium of stoichiometric InSb.

Let $N(x,t)$ be the number of diffusing In atoms (excess to 50% concentration) per unit volume at the position x measured from the opening along the capillary and the time t , D , the coefficient of diffusion. The initial condition is simply $N(x,0) = 0$, and the boundary condition at the opening $x = 0$ is $N(0,t) = N'$. The value of N' can be found by requiring a stoichiometric eva-

poration, that is,

$$\frac{E_{In}}{E_{Sb}} = \frac{W_{In}}{W_{Sb}} \frac{P_{In}}{P_{Sb}} \left(\frac{M_{Sb}}{M_{In}} \right)^{3/2}$$

$$M_{In} \doteq M_{Sb}, P_{In} \doteq 1\% P_{Sb}, W_{In} \doteq 100 W_{Sb}$$

hence $N' \doteq W_{In} - W_{Sb} = 99\% N^*$

where N^* is the number of atoms per unit volume in stoichiometric InSb. The diffusion flow $J_D = -D \partial N / \partial x$, together with the forced flow $J_v = -Nv$ which is in the negative X-axis direction, give the combined flow

$$J = -D \partial N / \partial x - Nv$$

The equation of continuity offers a time dependent relation here, that is

$$\partial N / \partial t + \partial J / \partial x = 0$$

or $\partial N / \partial t = D \partial^2 N / \partial x^2 + v \partial N / \partial x$

The boundary conditions are

$$N(x, 0) = 0, N(0, t) = N'$$

The solution⁽²⁾ is found to be

$$N(x, t) = \frac{1}{2} N' \exp(-v/D x) \left\{ \left(1 - \operatorname{erf} \frac{x-vt}{2\sqrt{Dt}} \right) + \exp(v/D x) \left(1 - \operatorname{erf} \frac{x+vt}{2\sqrt{Dt}} \right) \right\}$$

where $\operatorname{erf}(y) = \frac{2}{\sqrt{\pi}} \int_0^y \exp(-z^2) dz$

Since $\operatorname{erf}(-y) = -\operatorname{erf}(y)$, $\operatorname{erf}(0) = 0$, $\operatorname{erf}(\infty) = 1$, the foregoing equations yield, as a limiting value,

$$\begin{aligned} N(x, t) &\leq \lim_{t \rightarrow \infty} N(x, t) = \frac{1}{2} N' \exp(-v/D x) \left\{ (1+1) + \exp(v/D x) (1+1) \right\} \\ &= N' \exp(-v/D x) \end{aligned}$$

As a typical case, consider the evaporation of 300 mg InSb over a period of 50 minutes. If the dimensions of the capillary are: Diameter = 0.04 cm,

... in a ...

(2) B. I. Boltaks, "Diffusion in Semiconductors".

Length = 0.4 cm, then v is approximately 0.02 cm/sec. For the temperature range not too higher than the melting point of InSb (i.e., in the normal range of crucible temperatures), D is of the order of 10^{-4} cm²/sec. Upon substitution of all these numerical values into the expression $N(x,t) = N^* \exp(-v/D x)$, it is seen that

$$N(x=0.4 \text{ cm}) \leq N^* \exp(-80) < N^* 10^{-32}$$

This indicates that with reasonably attainable parameters diffusion flow has a negligible effect on the flow.

RESULT AND INTERPRETATION

In early experiments a quartz crucible with the top completely sealed was used to determine whether or not the vapor pressure inside the crucible is sufficient to push the melt out through the capillary. It was found that molten InSb does not wet quartz, and further that when the temperature of the crucible is raised sufficiently so that the liquid is forced through the capillary, the flow is always too fast for practical use. This is owing to the effects of low friction and large angle of contact between the melt and the quartz. This discontinuity of flow can be completely eliminated by using a tantalum crucible, which is wetted to some extent by In-Sb mixture.

A crude crucible was made of tantalum with the following characteristics (Two-electrode model):

1. The crucible was made of tantalum tubing with a wall thickness of about 0.005".
2. The capillary part was made by squeezing the bottom part of the crucible.
3. The evaporating boat was formed by extending the squeezed part of the crucible and narrowing the section near the opening of the capillary.

4. A graphite lid was made to fit the top of the crucible. (The resulting seal was not perfect.)

In use, the crucible was maintained at uniform temperature of about 800°C by passing current through it. The same current passed through the narrow part near the opening of the capillary (i.e. the boat), maintaining it at a sufficiently high temperature that the effluent evaporated rapidly.

Using the above mentioned tantalum crucible as a constant vapor source, a set of five successive films was produced without changing the temperature. The total amount of InSb in the crucible was 270 mg. The following measurements of the films were obtained after they were annealed for a few hours at 200°C:

Film	Type	Thickness(A)	Conductivity(ohm-cm) ⁻¹	Hall Coefficient(cm ³ /coul)
I				Not measurable
II	n	2600	3.8	11
III	n	1200	2.8	36
IV	p	900	2860	0.0095
V				Not measurable

It is normally expected that the first material evaporated will be Sb rich, because some time is required for the evaporating liquid outside the capillary to come to equilibrium. It is also expected that the last part to be evaporated will be In rich, because it contains the In-rich residue that is left after the supply in the boat is exhausted. These effects are enhanced by use of a small crucible charge. This accounts for the radical non-stoichiometry of the first and fifth films. The measurements of the other films, particularly the presence of a measurable Hall coefficient, indicates

that they are nearly stoichiometric. Thus, even though the crucible was not completely sealed, so that there was a chance for escape of non-stoichiometric vapor and that non-stoichiometric condensation might occur in the upper part of the crucible (which was a little cooler than the bottom), and that some contamination was probably introduced by handling the home-made crucible, the measurements of these films indicated that the present method is practically workable. The relatively low conductivities and high Hall coefficients of the n-type Film II and Film III indicated they have a little excess of Sb which served as donor-type impurities. The high conductivity and low Hall coefficient of the p-type Film IV indicated that near the end of the evaporation, the melt in the crucible was becoming non-stoichiometric with an excess of In due to the Sb-rich vapor lost and the non-stoichiometric condensation at the top of the crucible.

It was expected that, if no non-stoichiometric vapor were lost and if there were no non-stoichiometric condensation at the top of the crucible, a much better set of films could be produced. An improved four-electrode model crucible was designed for this purpose. It was made of tantalum, and was similar to the two-electrode one except for the following differences:

1. The top was sealed completely with a spot welder so that there was no vapor lost at the top.
2. In extending the top of the crucible to the electrode, the part near the top was narrowed such that the temperature of the top of the crucible was nearly the same as that of the bottom. This reduced the non-stoichiometric condensation inside the crucible greatly.
3. Two more electrodes were connected to the narrow part at the opening of the capillary. This provided an independent control of the temperatures of the

crucible and of the hot evaporating region.

A set of eight films was produced with the four-electrode model crucible. The total amount of InSb was about 800 mg. The following measurements were made after the films had been annealed for 12 hours at about 200°C.

Film	Type	Thickness(A)	Conductivity(ohm-cm) ⁻¹	Hall Coefficient(cm ³ /coul)
I	n	740	6.14	0.216
II	n	1550	1.98	137
III	n	960	6.3	43
IV*	p	2600	39.8	1.8
V	n	2500	9.5	68
VI	n	1940	1.31	71
VII	n	2260	0.237	26
VIII	--	Not measurable	--	--

Evidently, the above results offer strong support to the method suggested here.

CONCLUSION

Since the whole argument is not limited to any particular compound or alloy, it is concluded that it is both theoretically and practically true that the present method can be used to provide a constant stoichiometric vapor source for any compound and alloy. It is also evident that a large amount of material can be used at one evaporation and the rate and the temperature of evaporation can be changed with little effect on the stoichiometry of the vapor except in the short duration of changing temperature.

* Evaporation was stopped for a short time between films III and IV. This no doubt explains the deviation of the properties of Film IV.

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It is well known that fractional distillation of the evaporant is the greatest difficulty in making alloy films by vacuum evaporation. A single-source technique that avoids this difficulty is described here, and the result of a successful trial of the technique is presented.

The vapor source designed for this purpose consists of three parts: the crucible, the crucible heater, and the boat. The charge in the crucible is kept in the liquid state by the crucible heater. The crucible is completely sealed except for a capillary at the bottom which extends to a small opening at the hot evaporating boat. The pressure inside the crucible, which is controlled by the crucible heater, can be adjusted to give an appropriate flow of charge through the opening. As the material in the boat evaporates, it is constantly replenished by stoichiometric mixture from the crucible. It approaches a steady state composition such that the composition of the material leaving the boat, i.e., the vapor, is the same as that of the material flowing into it.

Care is taken to keep the crucible at a uniform temperature so that there is no non-stoichiometric condensation inside the crucible. The diffusion problem is considered theoretically. It is shown that with practically attainable capillary dimensions and flow rates, the effect of diffusion is negligibly small.

The suggested technique has been tested by using a crude crucible which has the main characteristics proposed here. The results support the present method strongly.