

Evaporation characteristics of Sb thin films in the vicinity of St707 getter material

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A model is presented that describes the pumping characteristics of St707 getter material, the evaporation rate of antimony, and the resulting partial pressure of Sb within a vacuum chamber. The results show that within the 250-450°C range, the partial pressure of antimony ranges from 10^{-7} Pa to 10^{-2} Pa. In a limiting case where the getter efficiency is tuned to 10,000 L/s, partial pressures are still just barely breaching UHV boundaries (about 10^{-7} Pa). Thus, the getter has little effect with respect to Antimony evaporation due to the dominating Sb recombination rate term.

I. INTRODUCTION

Antimony is a common dopant in fast semiconductor technology, and is an often talked about topic in nanoscale electronics. However, detailed descriptions of evaporation rate, sticking coefficient, and other properties have been largely left unstudied.

At the University of Chicago, the fabrication of large area photo detectors requires a detailed knowledge of antimony, specifically how it behaves when in the vicinity of getter material. The motivation for this study is to fully characterize the antimony thin film for use in photo cathode and photo detector production.

In the following sections, we will form a model that describes what we believe to be the relevant evaporation characteristics of Sb thin films. At the moment, a possible failure point for photo tube production is the loss of antimony photo cathode material as well as the partial pressure of antimony inside the tile during the activation of the getter. The results of this paper provide evidence that suggests that the partial pressure of antimony is well maintained by its condensation rate, and may not be a concern.

To aid in removing free gases within the photo detector, we introduce an St707 non-evaporable getter (NEG) material. The pumping speed of the getter was thought to be an relevant factor for determining the partial pressure of Sb. Results show that this may not be the case. In what follows, we provide a characterization of getter pumping speeds at various activation temperatures and durations. The results of this paper should motivate the need for further experimentation.

II. THEORY

We first describe a model which can be used to estimate the characteristics of both the antimony layer and

the getter material. This involves three key values: the evaporation rate of Sb, the pumping speed of the getter, and the rate at which Sb atoms recombine with the film.

A. Partial Pressure of Sb

The partial pressure of antimony within a small chamber must be related to the evaporation rate from the Sb surface, the pumping speed from an external sink (getter material), and the rate at which Sb molecules kinetically recombine with the coated surface. The relationship can be derived from,

$$P = \frac{Q}{S} \quad (1)$$

where Q is the rate at which gas enters a chamber and S is the rate at which gas leaves. For our system, we use this to specify the partial pressure of antimony, \mathcal{P}_{sb} :

$$\mathcal{P}_{sb} = \frac{P\dot{V}}{S_g + S_{film}} \quad (2)$$

where $P\dot{V}$ represents the rate at which antimony evaporates from the film surface, S_g is the pumping speed of the getter, and S_{film} is the rate at which molecules condense or recombine with the Sb surface.

We start by finding an expression for the evaporation rate, $P\dot{V}$. In a perfect vacuum, the molar flux of substance that leaves a surface is found from the Hertz-Knudsen equation^{2,3}.

$$\dot{n} = \frac{Ap^\circ}{\sqrt{2\pi MRT}} \quad (3)$$

where A is the surface area of the film, p° is the vapor pressure of the substance, M is the molecular mass, R is the universal gas constant, and T is the temperature of the surface. Substituting into the ideal gas law, we find $P\dot{V}$

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$$P\dot{V} = \dot{n}RT \quad (4)$$

$$= p^\circ \sqrt{\frac{RT}{2\pi M}} \quad (5)$$

Often times, the Hertz-Knudsen equation is corrected for non-perfect vacuum by subtracting \mathcal{P} , the pressure above the evaporating surface. However, this correction is accounted for by the condensation rate S_{film} in equation 2. The approximation as a perfect vacuum for $P\dot{V}$ then remains valid.

The vapor pressure of Antimony as a function of temperature is linear. Empirical data was tabulated and fitted to find the relationship,

$$\log[p^\circ] = 13.664 - \frac{11025}{T} \quad \text{Pa} \quad (6)$$

for temperature T in Kelvin.¹¹ Figure 1 shows a plot of the evaporation rate, $P\dot{V}$.

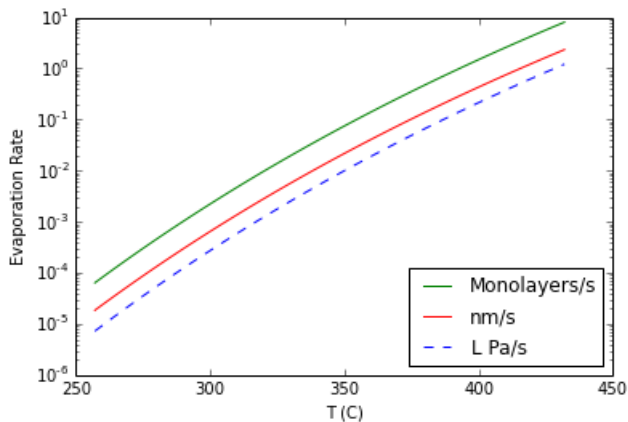


FIG. 1. Evaporation rate, or $P\dot{V}$, for Antimony as a function of temperature (blue). The green and red curves represent Monolayers/s and nm/s rates respectively for an 8×8 inch film.

Next, to find the rate at which Sb atoms recombine with the film surface, we use an argument involving the kinetic theory of gases⁴. The rate at which atoms strike and stick to the Sb surface is proportional to the surface area A , the sticking coefficient K_{stick} , as well as the molar flux density $n\bar{v}/4$. In terms of ideal gas constants,

$$S_{film} = (A/4) \sqrt{\frac{RT}{2\pi m}} K_{stick} \quad (7)$$

where the factor of 4 comes from an averaging over half of all solid angle (a surface covering the plane of the film). Our concern in the current paper is the condensation of antimony back onto the original Sb film, and thus the sticking coefficient K_{stick} refers to antimony-antimony attraction. Further investigation should be dedicated to

exploring the properties of Sb condensing onto other surfaces such as Al_2O_3 or MgO , which would involve different sticking coefficients.

Experiments that attempt to measure K_{stick} can be found in references by Bennett, Kitagawa, and Metzger.^{5,6,7} However, these studies all involve semiconductor electronics at much higher temperatures than considered here (Bennett uses 700-1000C). Still, from Bennett's thorough formulation, we can interpolate the sticking coefficient expression to lower temperatures (figure 2). As is shown, the self sticking coefficient of antimony is ≈ 1 .

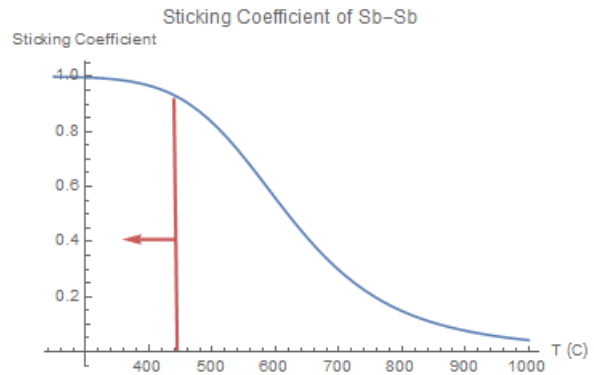


FIG. 2. Sticking coefficient of Sb to Sb as formulated by reference 5. The red vertical bar indicates our temperature range of interest

We now attempt to describe the properties of the getter, specifically the pumping speed $S_g(T, t_a)$.

B. Getter Pumping Speed

The SAES St707 non-evaporable getter is a Zr-V-Fe alloy that, when activated at temperature T for time t_a , acts as a compact pumping mechanism in high vacuum. To find the pumping speed, we start by assuming that for each molecule on the getter surface, there is a probability to transition into the interior of the material.

This can be visualized statistically as a layer of passive molecules on the surface occupying state "A". At a threshold amount of energy, these molecules are allowed to transition to state "B" (see Figure 3).

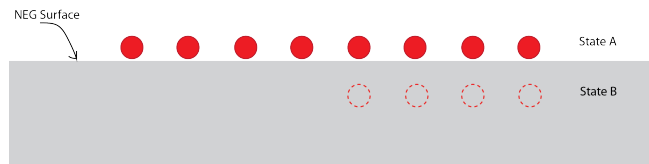


FIG. 3. A passive layer of Sb molecules on the surface of the getter is allowed to transition into the "B" state with a statistical probability proportional to the activation time and activation energy

We approximate the fraction of the molecules that transition from state “A” to “B” in time t_a to be $(1 - e^{-\gamma t_a})$. This term can be thought of as the getter efficiency, which increases with the factor γ . We can multiply this getter efficiency with the maximum getter pumping speed S_{max} to find the total pumping speed.

$$S_g(T, t_a) = S_{max}(1 - e^{-\gamma t_a}) \quad (8)$$

The factor γ then must depend on the temperature of the molecules in state “A”, as well as the minimum energy needed for a transition from state “A” to “B” (activation energy E_a). In fact, γ should be equivalent to the average number of molecules with energy E_a . Using Maxwell-Boltzmann statistics,

$$\gamma = \frac{N}{Z} g_i e^{-\frac{E_a}{k_b T}} \quad (9)$$

$$= k_0 e^{-\frac{E_a}{k_b T}} \quad (10)$$

for

$$N = \sum_i N_i \quad Z = \sum_i g_i e^{-\frac{\epsilon_i}{k_b T}} \quad (11)$$

where N is the total number of molecules in state “A”, Z is the partition function, k_b is the Boltzmann constant, and T is the activation temperature. We set $\frac{N}{Z} g_i = k_0$ for fitting purposes, as this factor is a constant.

Plugging in γ , we get

$$S_g(T, t_a) = S_{max}[1 - \exp(-t_a k_0 e^{-\frac{E_a}{k_b T}})] \quad (12)$$

C. Fitting the getter data

The getter pumping speed derived in the previous section has three unknown parameters. Literature describing the characteristics of the St707 NEG are seemingly contradictory^{8,9,10}. Therefore, in an attempt to stay consistent, we only reference data described by the St707 SAES brochure.¹

To find the parameters k_0 and E_a , we fit the distribution described above (12) to the getter efficiency S_g/S_{max} . Thankfully, the brochure provides an estimated efficiency value for various activation times and temperatures. The fit results were consistent, and after averaging over five data points, the results are:

$$E_a = 6.929 \times 10^{-20} \text{ J} \quad \approx 0.5 \text{ eV} \quad (13)$$

$$k_0 = 4.6 \quad (14)$$

For S_{max} , we use a value of 5.93 L/s based on the maximum pumping speed conditions described in figure 3 of the brochure. But because this quantity is critical

and not clearly stated by SAES, we treat this as a tunable parameter to be clarified by future experimentation.

Furthermore, the five data points used to find E_a and k_0 were found “by eye”, as the plots provided in the brochure are non numerical. The error associated with these values should be a concern to the reader, even though they look to be of the correct order of magnitude. Further experimentation could greatly improve upon this error.

The results for $S_g(T, t_a)$ are found in the set of curves displayed in figure 4. In general, these distributions correctly outline the qualitative getter characteristics described by the manufacturer. Considerable intuition can be built by examining the interactive plots found at <http://psec.uchicago.edu/library/evapmath.php>.

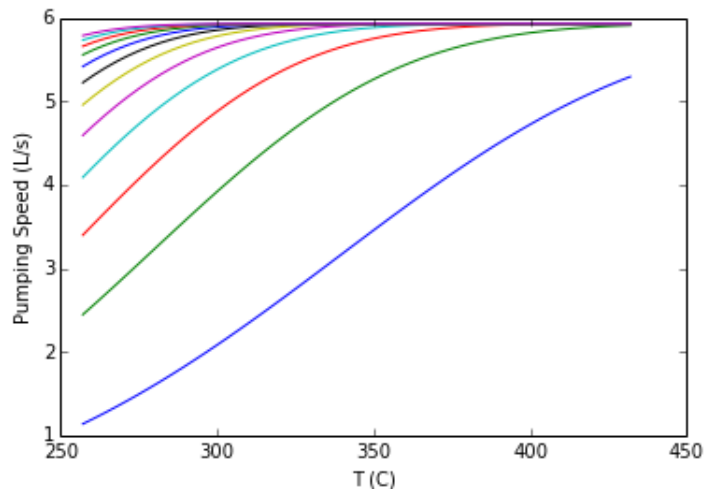


FIG. 4. Pumping speed as a function of activation temperature. Colors blue up to violet represent different activation times from 10 minutes (blue) to 3 hours (violet) in increments of 15 minutes. See <http://psec.uchicago.edu/library/evapmath.php> for an interactive plot.

D. Results and Discussion

We have successfully acquired expressions for each unknown quantity in

$$\mathcal{P}_{sb} = \frac{P\dot{V}}{S_g + S_{film}} \quad (15)$$

The plotted results are found in figure 5. As a consequence of high evaporation rate and recombination rate, the getter material contributes a negligible degree of pumping speed on the Sb gas. If the fit parameters are taken to be correct, the condensation rate S_{film} dominates.

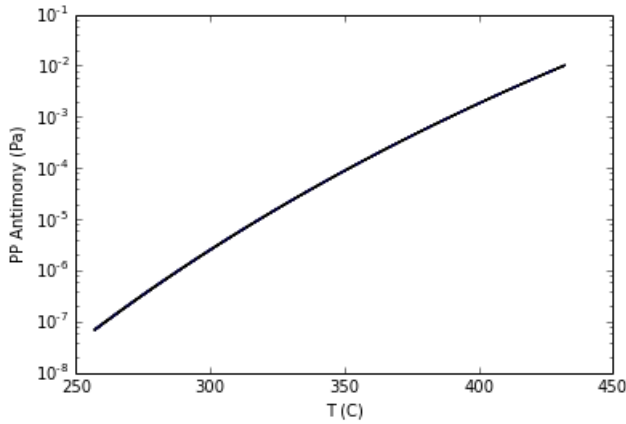


FIG. 5. The partial pressure of Antimony in the tile as a function of temperature. The single line distribution shows that the getter material contributes a negligible amount of pumping speed to the system. The recombination of the Antimony atoms to the film dominates the partial pressure.

During photo tube fabrication, we are concerned both with the loss of antimony photo cathode material and with the cleanliness of the other pristine internals. In an ideal situation, the partial pressure of antimony would be zero. Because the partial pressure is well regulated by the recombination rate, the characteristics of the getter become irrelevant. However, the outgassing rates of other materials within the tile still may require the getter material for regulation. This model can be used as a general description of the getter activation, and is not tied down to studies of antimony thin films.

III. CONCLUSIONS

The characteristics of the St707 getter are important for determining the partial pressure of antimony. Unfortunately, these characteristics are highly uncertain and beg for experimentation. Simple experiments for measuring the pumping speed of the getter material at various activation times and temperatures are in development at University of Chicago.

The data shows that the getter has little effect on the partial pressure of Antimony; the antimony will do what it pleases regardless of a present getter material. How-

ever, it is yet to be determined whether or not these partial pressures are acceptable for the UHV levels desired during MCP photo tube production. Thankfully, the data is only concerned with baking procedures. Under normal fabrication conditions, pump down will occur mainly at room temperature where the vapor pressure of antimony is negligible.

IV. ACKNOWLEDGEMENTS

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