Flux Calibration of Ti-Ball Ti Source for Precision Deposition of Barium Titanate

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Abstract —

A Ti-Ball titanium sublimation source was calibrated to atomic flux for use in molecular beam epitaxy (MBE) growth of thin films. Precise calculations of atomic flux are necessary for growth of crystalline barium titanate (BTO) films as well as measurements of the sticking coefficients (σ) to better understand the mechanism of crystal growth. Two sources used for flux calculations, film growth rate and manufacturer supplied total sublimation rate, disagreed by an order of magnitude, requiring additional inquiry into the source of error; however, both calculations agreed that σTi >> σBa in growth of BTO.

I. INTRODUCTION

Barium Titanate (BTO) is a multifunctional oxide material with ferroelectric and thermoelectric properties, among others [1]. These properties make it an important layer for developing multilayer heterostructure in next generation multifunctional sensors [2]. Crystalline thin film growth of BTO is important for holding the desired ferroelectric or thermoelectric properties; however, without tight control over the atomic fluxes of both Ba and Ti to assure a 1:1 atomic ratio within the lattice, thin films grown by molecular beam epitaxy (MBE) will form amorphously [3]. Ba is deposited through the use of an effusion cell, whose surface flux is easily calculated by Equation 1, seen below.

$$\Phi = \frac{3.51 * 10^{22} PA}{\pi L^2 \sqrt{MT}} \qquad \text{Eq. (1)}$$

Where Φ is atomic flux (atoms/cm^2-s), P is the vapor pressure of Ba (Torr), A is the aperture area (cm^2), L is the distance from the source to the substrate (cm), M is the molecular weight (g/mol), and T is the temperature (˚C) [2]. The Ti is deposited by sublimation from a hemispherical mini Ti-Ball source whose sublimation rate is only controllable by applied current. While the manufacturer of the Ti-Ball (Varian Vacuum Technologies) provides an approximate sublimation rate for a current level, an atomistic flux function must be determined to fully control growth [4]. In addition to greater control over the crystallinity, an exact value for atomic flux will allow for calculations of sticking coefficients (σ) of Ti during BTO growth, which will help determine the mechanistic properties of growth [5]. These experiments aim to calculate the atomic flux by growth of a Ti thin films on a cleaned germanium (Ge) sample.

II. METHODS

Ge was cleaned by degreasing in heated trichloroethylene, acetone, and methanol followed by drying with an argon gas source. After this cleaning procedure, the Ge substrate was adhered to a molybdenum puck using silver paste, then the puck was inserted into the vacuum chamber. Once a pressure of 10^{-9} Torr was achieved, X-Ray Photoelectron Spectroscopy (XPS) was performed using a magnesium anode to determine the initial atomic surface characteristics. A full sweep from 1100-0 eV was performed first, followed by tight scans around the characteristic binding energy peaks for Ge 3d^5 (39-25 eV), C 1s (293-274 eV), and Ti 2p^3 (470-449 eV).

A. Ti Growth

Ti growth was performed in a growth chamber with the substrate at room temperature (to assure $\sigma_{Ti} \sim 1$), an initial pressure of 10^{-9} Torr, and the substrate placed 7" (17.78 cm) away from the Ti-Ball. Ti was grown at five current values spanning the nominal operating range of 35-45 A. Higher current values were operated for shorter time lengths to reduce any risk of the Ge signal disappearing entirely.

Table 1: Growth Time for Applied Currents

Ti-Ball Applied Current (A)	Growth Time (min)
35.0	20
37.5	20
40.0	15
42.5	10
45.0	5

B. Analysis

Upon completion of the growth, XPS was again performed on the substrate to determine any change in surface atomic composition. As the Ti film layer increases in thickness, the signal for the Ge base will become smaller. This decrease in signal, or attenuation, was calculated using Equation 2, shown below.

$$Attenuation(\%) = \frac{A_{post\ growth}}{A_{pre\ growth}} * 100\% \qquad \text{Eq. (2)}$$

Where A is the area under the curve of the XPS scan. All areas were measured using the Mulitpak software. Using the NIST EAL13 software, the attenuation of Ge through a layer of Ti was directly related to film thickness through the kinetic energy of the Ge photon, the asymmetry factor of Ge, and the absorption characteristics of Ti [6]. Dividing the film thickness

by the growth time then gave the growth rate of each current level.

To calculate the flux at the surface, several assumptions were made: First, due to the lower temperature $\sigma_{Ti}=1$; second, flux was uniform across the area of the sample; third, all Ti growth was crystalline. To calculate flux, growth rate must be multiplied by the atomic density of the film; because crystalline Ti is hexagonal close packed in structure with 6 atoms per unit cell and a unit volume of $1.06*10^{-22}$ cm^3, crystalline Ti has an overall atomic density of $5.65*10^{22}$ atoms/cm^3 [7]. Multiplying each of the growth rates by this atomic density allowed for a curve-fitting function to be developed to map the atomic fluxes within the operating range of the Ti-ball.

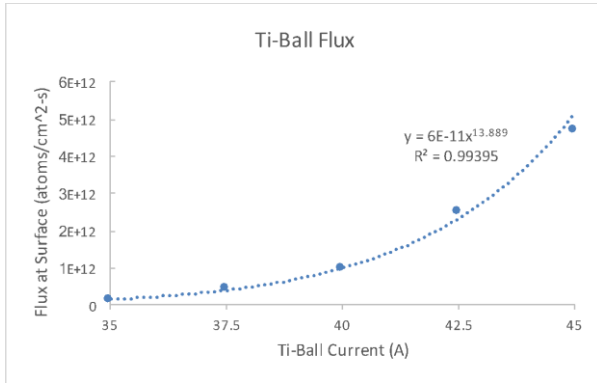## III. RESULTS

The atomic flux fit is shown in Figure 1:

Fig. 1: A power fit of the flux best predicts the data

It shows that $\Phi_{Ti}=5.67*10^{-11}(I)^{13.889}$ within the Ti-Ball operating range, where I is the applied current in A.

A. Generalization of Flux

Assuming a steady state system, no secondary source of Ti generation, and a purely hemispherical surface with no significant defects allows for one to equate the surface flux between two surfaces, as represented by Equation 3, shown below.

$$\Phi_A r_A^2 = \Phi_B r_B^2 \qquad \text{Eq. (3)}$$

Combining Equation 3 with the value of Φ_{Ti} gives Equation 4.

$$\Phi(I,r) = \frac{\Phi_o(I)r_o^2}{r^2} = 5.67*10^{-11}I^{13.89}\left(\frac{r_o^2}{r^2}\right) \qquad \text{Eq. (4)}$$
$$= 1.792*10^{-8}\left(\frac{I^{13.89}}{r^2}\right)$$

Where r is the distance from the center of the Ti-Ball to the substrate (cm), r_o is the distance used in experimentation (17.78 cm), and Φ is the Ti flux (atoms/cm^2-s).

B. Comparison to Provided Values

The sublimation data provided by Vernier was translated into a flux by assuming a perfect hemisphere. At $r=r_o$ the Ti would be evenly distributed along a hemisphere of radius r_o, thus

$$\Phi = \frac{R_{sub}*N_A}{2\pi r_o^2 * MW * 3600} \qquad \text{Eq. (5)}$$

Where R_{sub} is the sublimation rate (in g/hr), N_A is Avogadro's number, and MW is the molecular weight of Ti. The expected flux was graphed against the calculated flux on a logarithmic scale.
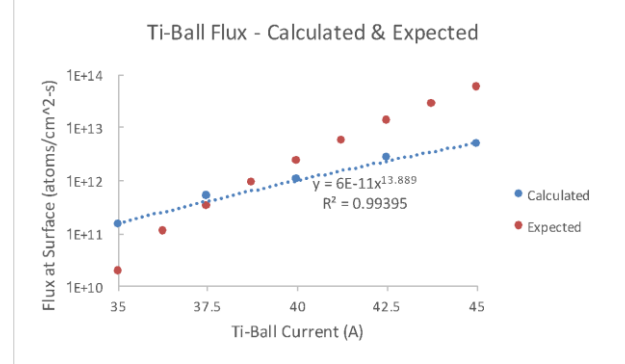

Fig. 2: Calculated Ti-Ball flux severely below the estimated expected values from manual

The magnitude in difference between the calculated flux and the estimation for the expected values shows that at least one assumption during either flux calculation was not valid.

C. Evaluation of σ Values During BTO Growth

Because of the order of magnitude difference between the calculated and expected results, σ evaluation was performed using the calculated results as a lower bound and the expected results as an upper bound. While the exact values of σ cannot be determined without precise knowledge of the number atoms of each element in BTO, a relationship between σ_{Ti} and σ_{Ba} can be determined using the molar fraction of Ba to Ti in the film and the fluxes of each to find a ratio.

$$\frac{\sigma_{Ti}\Phi_{Ti}}{\sigma_{Ba}\Phi_{Ba}} = R_m \qquad \text{Eq. (6)}$$

Where R_m is the molar ratio present in the BTO film. Using data collected by Northeastern Doctoral Student Sue Celestin during BTO growth, a substantial range of sticking coefficient ratios were observed utilizing the same substrate temperature, as summarized in Table 2.

Table 2: Values to Calculate Sticking Coefficient Ratios [8]					
Φ_{Ba}	$\Phi_{Ti,Calc}$	$\Phi_{Ti,Expect}$	R_m	σ_{Ti}/σ_{Ba}	
atom/cm^2-s	atom/cm^2-s	atom/cm2-s	Ti/Ba	Max	Min
1.30E+15	4.46E+12	3.96E+13	0.51	147	17
9.40E+15	4.46E+12	3.96E+13	1.20	2539	286
8.00E+14	4.46E+12	3.96E+13	1.67	299	34
1.30E+14	4.46E+12	3.96E+13	3.33	97	11

These show that even when considering Φ_{Ti} at the maximum flux value, Ti is orders of magnitude more likely to stick than Ba.

IV. CONCLUSIONS

Several assumptions must be audited in order to fully understand the root cause in the large difference between the expected and calculated flux levels. The first, and most likely cause in the disparity, is that the sublimation rate is not constant over both the area of the substrate and over the time of the growth. Time difference in the flux, for instance during a warm-up period, would greatly reduce the average flux experienced by the higher current growth periods due to the smaller time frame. This error could be reduced by increasing the time of all growths to a standard time period.

Another assumption in need of reevaluation is that Ti grows in its traditional crystal structure during the growth periods. The unit cell for Ti is 0.468 nm tall; however, some growths produced only 0.2-0.3 nm of film thickness. Non-crystalline growth would cause all flux calculations to be inaccurate. Using RHEED to monitor the crystallinity and growing for longer periods of time would give more credit to this assumption.

The third assumption to further investigate is the uniform and perfectly hemispherical sublimation by the Ti-Ball. While this assumption was made knowing there would be some variance between the calculated and actual results, any serious deformations or sublimation points not located on the hemispherical tip of the Ti-Ball could heavily skew the conversion from mass sublimation rate to atomic flux.

While the exact flux value will require further investigation, the sticking coefficient ratios confidently show that Ba flux must be much greater than Ti flux in order to achieve a 1:1 atomic ratio within crystalline BTO.

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BIOGRAPHY

Dalton Cox is a fifth year Chemical Engineering and Physics student with particular interest in Materials Science and Energy Technology. After graduation, he will be pursuing his doctorate in Materials Science.
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