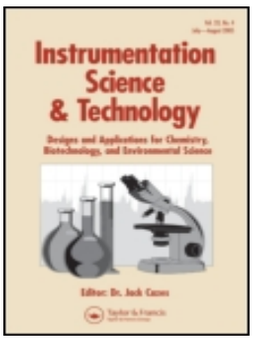

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EVAPORATION OF LOW-VAPOR PRESSURE METALS USING A CONVENTIONAL MINI ELECTRON BEAM EVAPORATOR

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□ *In this article, the evaporation of niobium, ruthenium, and titanium using a conventional mini electron-beam evaporator (*Tectraé-flux*) is described. These metals require high temperatures for evaporation due to their high melting points, low vapor pressures, and large bond energies between atoms. Usually, a high-power electron-beam evaporator with a power exceeding 600 W is used in order to grow films of these metals. However, evaporation conditions for deposition using a mini electron-beam evaporator of low power (600 W at 2 kV) were obtained. Film thicknesses between 2 nm and 12 nm were obtained and the films were characterized with different analytical techniques. In the case of ruthenium, a comparison between the evaporation achieved when using a graphite crucible or a metal rod as a target is presented. The quality of the deposited films was ascertained by Auger electron spectroscopy. Niobium and titanium film's thickness and quality were determined by X-ray reflectivity and atomic force microscopy. Theoretical values of vapor pressure as a function of temperature were calculated for niobium, ruthenium, and titanium using the Clausius-Clapyeron equation to compare their evaporation behaviors.*

Keywords e-beam evaporation, niobium, physical vapor deposition, ruthenium, titanium

INTRODUCTION

The technique of physical vapor deposition (PVD) is widely used for fabricating metal films by the evaporation in vacuum of many metals using a tungsten boat which is resistively heated or by using an electron beam (e-beam) system. These techniques are easy to operate and of low cost compared with others such as chemical vapor deposition,[1] sputtering,[2] or pulsed laser deposition.[3] When a reaction occurs between the tungsten boat and the molten metal, the use of a mini e-beam or e-flux evaporator is a good alternative. In conventional electron-beam evaporation process,

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electrons are released from a tungsten filament by thermionic emission. These electrons are accelerated towards a target maintained at a high positive potential producing high heating-power densities. The target can be a crucible containing the material to evaporate or the tip of a metal rod. The use of a crucible or a rod depends on the type of material to evaporate. For example, evaporation materials with low melting points such as aluminum, silver, or gold, which melt before reaching useful vapor pressures is obtained from a crucible. On the other hand, rod evaporation is used for refractory metals such as molybdenum, tantalum, and rhenium—in general, metals with melting point above 2123 K.[4]

Other electron-beam systems incorporate the use of magnetic fields to focus electrons directly towards the source material.[5] The problem of a mini e-beam evaporator of low power (600 W at 2 kV) arises when is necessary to evaporate metals of low vapor pressure (high melting point).[6] The vapor pressure or equilibrium vapor pressure is defined as the pressure exerted by a vapor in thermodynamic equilibrium with its condensed phase at a given temperature. The evaporation rate of a material under a given temperature depends on its vapor pressure.[7] Metals of low vapor pressure, such as niobium, ruthenium, and titanium, need to be heated at high temperatures to obtain a reasonable evaporation rate to fabricate the films. The beam power is mainly limited by the maximum operating voltage to accelerate the electrons thus high evaporation temperatures are achieved when the high voltage can operate between 2 and 10 kV.[8]

During the course of different experiments in our laboratory, thin films of Nb, Ru, and Ti are required. Consequently, a technique was developed to evaporate these metals using our *Tectrae-flux* mini e-beam gun. Before this work, there was no detailed information in the literature of how to perform evaporations of high meting point metals using a mini e-beam evaporator. The experimental setup and results presented here will help researches who need to perform similar evaporations without the need of a high-power e-beam gun.

EXPERIMENTAL

Instrumentation

The evaporation of Nb (99.9% purity), Ru (99.95% purity), and Ti (99.5% purity), all purchased from ESPI Metals, was performed in a vacuum chamber integrated with a *Tectrae-flux* mini e-beam gun (Figure 1a). The e-gun can reach a maximum power of 600 W at a maximum voltage of 2 kV. As can be seen from Figure 1, the e-beam gun is tilted at approximately 60° so the evaporated material can reach directly to the sample substrate, which is placed in front of the electron-gun. The

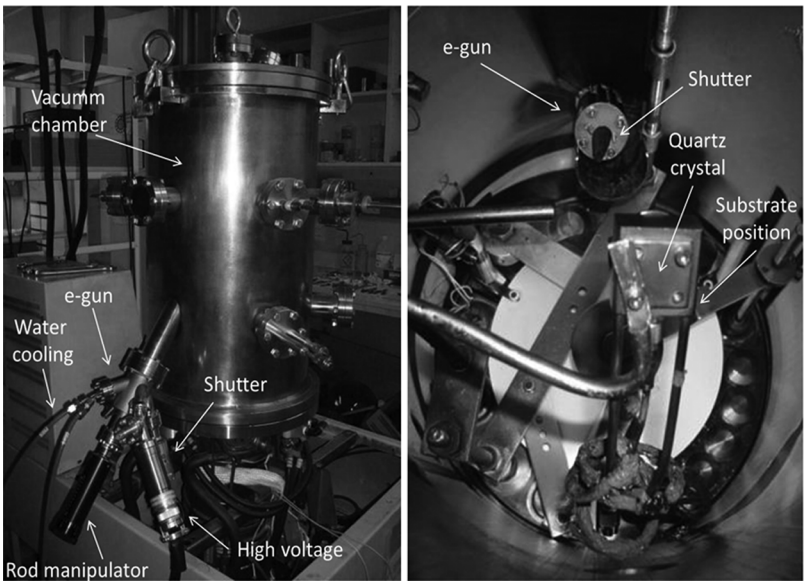

FIGURE 1 Images of the system used for electron-beam evaporation. The left image (a) shows the vacuum chamber integrated with a mini e-gun while the right image (b) shows a top view of the interior of the vacuum chamber. The electron-gun is oriented towards the substrate and quartz crystal microbalance head.

system operates at background pressure in the order of $7 \cdot 10^{-7}$ Torr. In Figure 1b, an image of the interior of the vacuum chamber from the top is shown. A quartz-crystal microbalance system (*SQM-160* from *MDC*) was used to monitor the thickness and deposition rate of the metal film. The substrates used were positioned immediately below the quartz crystal microbalance head. Both the crystal and the substrate were located in front of the e-beam gun, as shown in Figure 1b. The distance between the shutter of the e-gun and the position of the substrate was approximately 20 cm. The pressure of the chamber during the deposition of the metals was kept lower than $3 \cdot 10^{-6}$ Torr.

Film Characterization

The deposition of the films was performed on a (100) Si wafer substrate. Characterizations by X-ray reflectivity (XRR) and atomic force microscopy (AFM) were performed. The XRR pattern was taken at room temperature with a Bruker D-8 Advanced Diffractometer, using an X-ray tube with a copper anode ($\lambda(_{\mathrm{CuK}\alpha}) = 0.154$ nm). A simulation of the XRR pattern was performed using the Leptos software from Bruker Corporation. AFM images were taken in semi-contact mode with a silicon tip at 300 kHz and under atmospheric pressure using a NTegra Prima atomic force microscope from NT-MDT.

Evaporation using Graphite Crucible

For electron-beam evaporation, the crucibles used were made with materials of high melting points such as graphite (3925 K), tungsten (3695 K), and molybdenum (2896 K). Graphite crucibles were used because they did not react with the metal used for evaporation.

The material to be evaporated was introduced inside the graphite crucible positioned inside a coiled W filament. A voltage was applied between the crucible with positive potential and the W filament with ground potential. The filament was resistively heated and released electrons which were accelerated by a high voltage and impacted the graphite crucible, heating the crucible and the contained material. A schematic diagram of the mini electron-gun is shown in Figure 2.[6] A maximum accelerating voltage of 2 kV is possible to reach and emission currents up to 300 mA. Under these conditions, two problems may arise for the evaporation of low vapor pressure metals as Ti.[4] Ru, and Nb. First, no evaporation occurs or the evaporation rate is too low (< 0.01 Å/s), problem which can be solved by a higher power electron-beam gun. A vapor pressure of the material above 10^{-4} Torr is needed to reach a useful evaporation rate for the preparation of films. Second, the material may react with graphite when heated. For example, if Ru is evaporated using a graphite crucible, a compound of type $Ru_3(CO)_{12}$ can be formed. This compound, which has a melting point of just 497 K, becomes brittle and breaks during the evaporation process. Several Ru evaporations were performed using graphite crucibles. In all cases, the evaporation process was interrupted due to the breaking of the crucible.

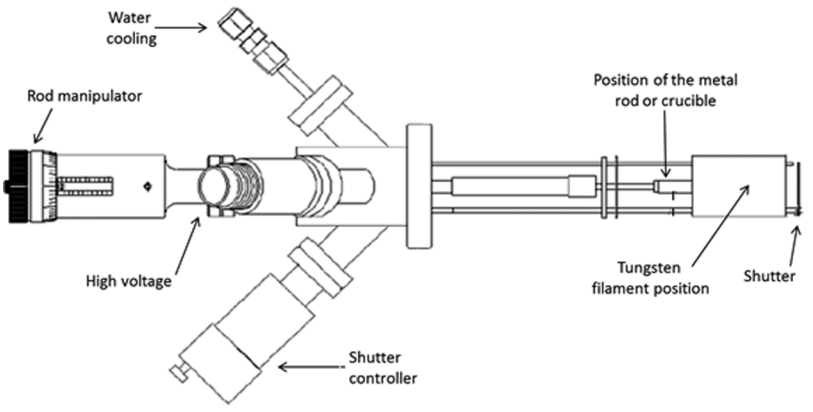

FIGURE 2 Representation of a mini e-gun. The graphite crucible can be replaced by a rod of the target material.

TABLE 1 Physical Data of the Evaporated Materials[9]

Metal	T to achieve a vapor pressure of 10^{-4} Torr	Melting point	Vapor pressure at melting point	$\Delta T^{(*)}$
Ruthenium	2533 K	2583 K	1.6×10^{-4} Torr	50 K
Niobium	2560 K	2741 K	4.5×10^{-4} Torr	181 K
Titanium	1726 K	1948 K	0.013 Torr	222 K

(*) ΔT corresponds to the difference between the necessary temperature to achieve a vapor pressure of 10^{-4} Torr and the temperature of melting point for a material.

Evaporation using a Metal Rod

Under this evaporation mode, the material in rod form is directly impacted by electrons, thus producing high heating-power densities rapidly. The films' purity was improved with the rod evaporation since the metal is the only material heated. The evaporation becomes more effective for materials such as palladium or Ti, which need a temperature lower than 1800 K to yield a vapor pressure of 10^{-4} Torr. However, the evaporation of materials such as Nb and Ru is still more difficult to achieve. In both cases, temperatures higher than 2500 K are necessary for reaching a reasonably vapor pressure, as shown in Table 1. In Figure 3, a plot of the vapor pressure as function of temperature determined from the Clausius-Clapeyron relation (Equation (1))[7] is displayed. The parameters T_0 and P_0 were found using experimental data for Ti, Nb, and Ru from Lide.[9] As one can be seen from the plots, titanium reaches a vapor pressure of 10^{-4} Torr at lower temperatures than Nb and Ru. These last metals

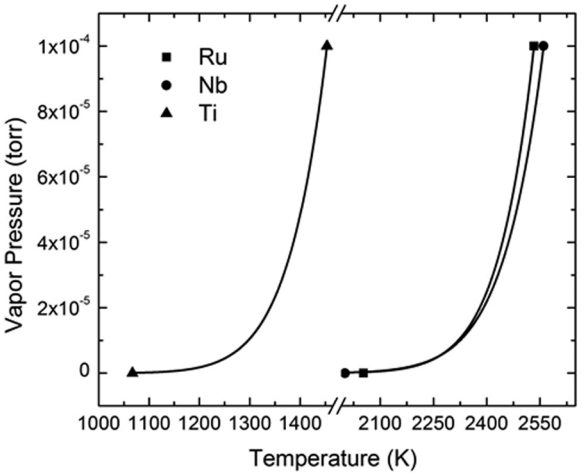

FIGURE 3 Vapor pressures of Ru, Nb, and Ti as function of temperature. The points correspond to experimental data while the continuous lines correspond to plots of the Clausius-Clapeyron curve.

present curves very similar (Figure 3), but as is shown in Table 1, Nb has a melting point 158 K higher than Ru, making its evaporation a bit more difficult:

$$P = P_O e - \frac{T_o}{T}, \tag{1}$$

The temperature difference (ΔT) between the melting point and the temperature needed to achieve a 10^{-4} Torr vapor pressure is an important consideration for the metal evaporation process. If this ΔT is sufficiently large, rod evaporation can be performed successfully because the temperature can be increased within this range in order to reach vapor pressures above 10^{-4} Torr. In this case, higher evaporation rates can be reached without risking material runoff from the rod tip which occurs when the melting temperature is suddenly reached in the metal. Ti and Nb present a ΔT wider than Ru (see Table 1). The evaporation of Ru was much difficult to perform by two reasons: first, because is not possible to make Ru wire and the dimensions of the rod made by casting Ru is not appropriated for our mini electron-beam gun. The Ru rods commercially found are too short (< 13 mm) or have diameters too large (> 6 mm).[10–12] Our electron-gun allows rod diameters from 1.5 mm up to 6 mm due to the 600 W power delivered by the power supply. Second, Ru presents a smaller ΔT than Nb (Table 1); thus a special attention must be taken to avoid reaching the melting point during evaporation and therefore, metal runoff inside the electron-gun. We could only commercially obtain Ru in shot a few mm in diameter. In the following section, a special setup is described used to perform evaporation of Ru shot.

RESULTS

Metals Evaporation

A photograph of Nb rod after evaporation is shown in Figure 4. The titanium rod showed a similar aspect after evaporation. In both cases, one end of the Nb and Ti rods (1.59 mm in diameter and 30 mmin length)

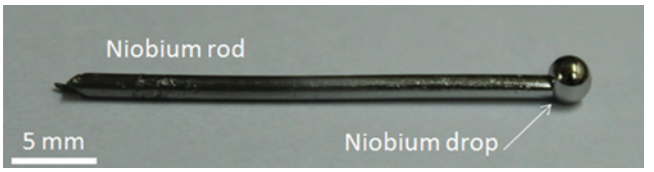

FIGURE 4 Image of Nb rod after evaporation. (color figure available online.)

was exposed directly to the electron-beam. This melted the metal forming a drop on the tip as shown in Figure 4. Nb and Ti presented a ΔT of 181 K and 222 K, respectively (see Table 1), so the filament current was increased in a wide range above the necessary temperature to reach a vapor pressure of 10^{-4} Torr without material runoff. A summary of the evaporation-deposition parameters used in these cases is tabulated in Table 2. In the case of titanium, an evaporation rate of 0.03 Å/s was obtained using a low emission current of 12 mA at 2 kV. Under these conditions, films thicker than 2 nm were obtained. The case of Nb was different, with a higher emission current of 50 mA at 2 kV, the maximum evaporation rate reached was only 0.01 Å/s. After depositing a 4 nm-thick Nb film, the position of the Nb rod inside the electron-gun had to be fitted constantly to maintain the evaporation rate and to get a larger film thickness. A total time of 5.7 h was necessary to grow a 12 nm-thick Nb film, as shown in Table 2.

The Ru evaporation technique was different. This metal cannot be found in rods with the dimensions required for our e-gun. Only Ru shot was available. For this reason, a graphite crucible was used in the first attempt to evaporate Ru. The evaporation-deposition conditions are summarized in Table 2. An evaporation rate that oscillated between 0 and 0.01 Å/s was achieved with an emission current of 240 mA operating the electron-gun at its maximum power. Under these conditions and after 4 h of evaporation, only a 2 nm-thick Ru film was deposited since the crucible broke due to the high temperature and the reaction between Ru and carbon.

A schematic drawing (not to scale) of the technique designed to directly evaporate the Ru spheres without using graphite crucible is shown in Figure 5. Two tungsten wires were wrapped around a W rod of 1.5 mm in diameter and 64 mm in length leaving two wire points to which a 3 mm diameter Ru sphere was spot-welded. Therefore, the Ru sphere was directly exposed to the e-beam and the metal would reach a higher local temperature thus achieving a higher vapor pressure and evaporation rate of Ru. A photograph recorded after evaporation was performed with this set-up is shown in Figure 6. Using this rod design, an 8 nm-thick Ru film was

TABLE 2 Parameters used during the Evaporation-Deposition of the Metals

	Niobium (rod)	Titanium (rod)	Ruthenium using graphite crucible	Ruthenium using new setup
Filament current	7.2 A	6.2 A	~8 A	7.4 A
High voltage	2000 V	2000 V	2000 V	2000 V
Emission current	50 mA	12 mA	240 mA	60 mA
Deposition rate	0.01 Å/s	0.03 Å/s	<0.01 Å/s	0.07 Å/s
Final Thickness	12 nm	2 nm	~2 nm	8 nm
Evaporation time	5,7 hrs	7 min	~4 hrs	20 min

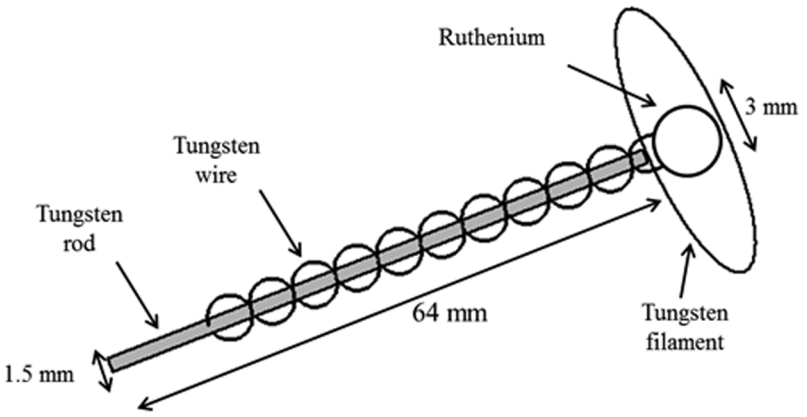

FIGURE 5 Scheme of setup designed for Ru evaporation.

deposited in just 20 min giving an evaporation rate of 0.07 Å/s, as shown in Table 2. In this case, special care was taken as the emission current increased because Ru has a ΔT value of only 50 K (see Table 1).

AES, XRR, and AFM Results

Using these evaporation techniques, two different samples were grown. The first sample was a film of Ru on a Pd foil. The second sample was a bilayer film composed by a Nb film and an underlying thin layer of Ti on top of a Si substrate.

An Auger electron spectrum of the Ru film is shown in Figure 7. Characteristic peaks of Ru were observed, in addition to a strong carbon peak and oxygen signal. Carbon and oxygen are typical residual contamination found on the surface of the Ru film because the Auger characterization was performed in a different vacuum system and the sample was exposed to ambient conditions.

The XRR pattern together with the fitted curve obtained for the bilayer Nb/Ti film is shown in Figure 8. A summary of the parameters used in the fitting (thickness, roughness, and density) are also shown in Table 3. Some differences between fitted thicknesses and the nominal values measured

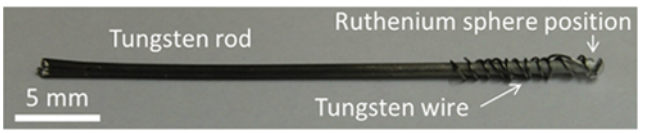

FIGURE 6 Image of the rod design for ruthenium evaporation recorded after its use. A tungsten wire was wrapped in a tungsten rod, and then a Ru sphere was spot welded in the wire. (color figure available online.)

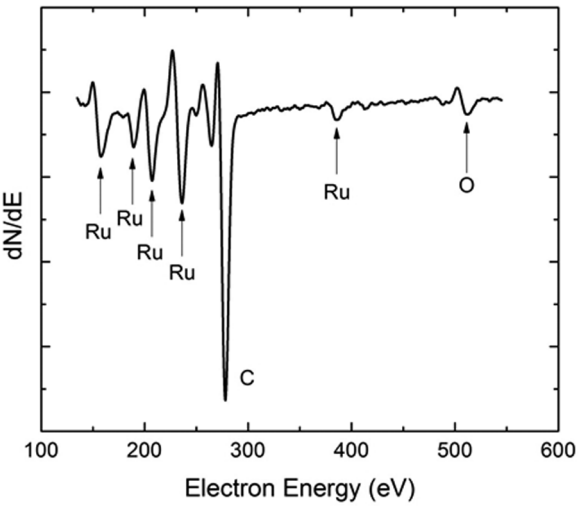

FIGURE 7 Auger electron spectrum of a Ru thin film deposited on a Pd foil.

during the evaporation using the thickness monitor (Table 2) are observed. In the case of Ti, 2 nm was measured during evaporation while 4.6 nm was obtained from the fitting of XRR, mainly due to the native oxide grown on the Ti film. In the case of Nb film, a thickness of 11.5 nm was determined from the XRR fitting, very close to the nominal 12 nm measured by the thickness monitor during its deposition. The fitting of the XRR curve was possible assuming a 9.7 nm niobium oxide layer a stoichiometry corresponding to Nb_2O_5 was on the surface of the Nb film. The formation of this native oxide was expected because this metal oxidizes easily under room

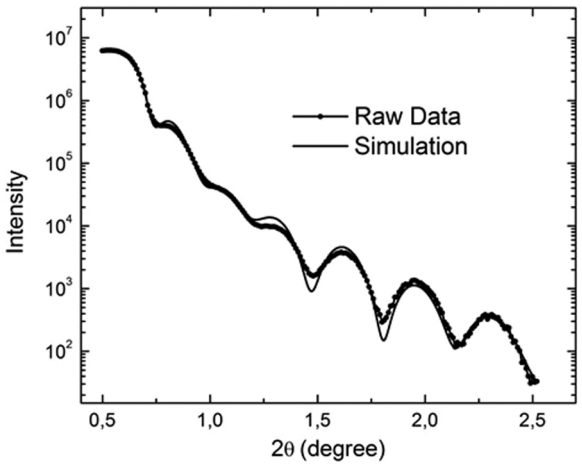

FIGURE 8 X-ray reflectivity spectrum of a bilayer sample of Nb/Ti deposited on a (100) Si substrate.

TABLE 3. Parameters Determined by XRR Fitting

	Thickness (nm)	Roughness (nm)	Density (g/cm^3)
Nb_2O_5	9.7	1.43	5.5
Nb	11.5	0.29	5.4
$Ti + TiO_2$	4.6	0.73	3.9
Si	—	0.74	2.1

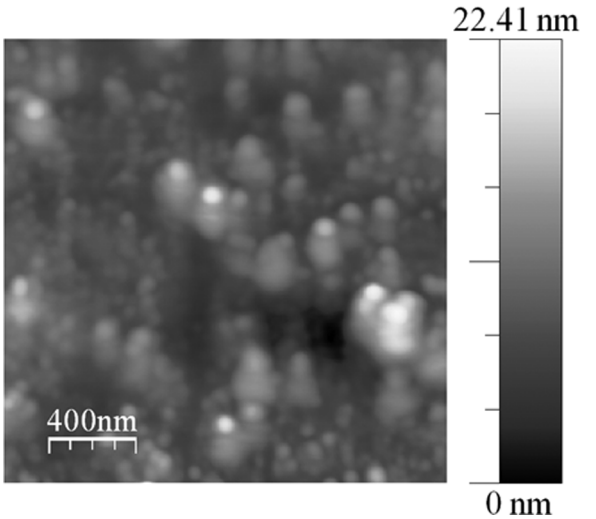

FIGURE 9 Atomic force microscopic image of a bilayer sample Nb/Ti deposited on a Si substrate.

conditions.[13] Finally, a total thickness of 25.9 nm of this bilayer sample was determined. Roughness values of 0.73 nm and 0.29 nm for the Ti and Nb layers, respectively, were determined, revealing the relatively good quality of the metal deposits in spite of the low evaporation rates used. A higher value for the Nb oxide roughness of 1.43 nm was obtained.

An AFM image of the bilayer sample surface is shown in Figure 9. The image was acquired scanning an area of 2 μm x 2 μm under the conditions detailed in characterization section. A well-defined equiaxial grains morphology mainly less to 100 nm is observed and attributed to the growth mode of the Nb on Ti layer. An average roughness of 1.9 nm and a total thickness of 22.4 nm were also determined from the image. Both values agreed with the values obtained from the XRR results.

CONCLUSIONS

The set-up and conditions have been described to evaporate three metals of low vapor pressure, Ti, Nb, and Ru, using a mini e-beam

evaporator of low power (*Tectraë-flux*). Ti and Nb films were deposited by evaporation from rods made of these materials mounted inside the electron-gun. Also, Ru shot was attempted to be evaporated by the electron-beam from a graphite crucible and later by implementing a rod design with a small Ru sphere spot welded to a W support rod. These results with the rod design yielded a higher evaporation rate of Ru and thus film growth of larger thicknesses in shorter times of evaporation. Good quality of the metal films deposited under these conditions was obtained as ascertained by AES, XRR, and AFM characterizations.

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REFERENCES

1. Park, J. H.; Sudarshan, T. S. *Chemical Vapor Deposition*; ASM International: Ohio, USA, 2001.
2. Wehner, G. K. Controlled sputtering of metals by low-energy Hg Ions. *Phys. Rev.* **1956**, *102*(3).
3. Lowndes, D. H.; Geohegan, D. B.; Puretzky, A. A.; Norton, D. P.; Rouleau, C. M. Synthesis of novel thin-film materials by pulsed laser deposition. *Science* **1996**, *273*(5277), 898–903.
4. http://www.e-beam-evaporator.com/e-flux.pdf, Tectra GmbH Physikalische Instrumente, 2013.
5. http://pst4thinfilm.de/index.php?id=32&L=1,Plasma & Semiconductor Technologies GmbH, 2013.
6. Ribbe, A. E. Cost effective upgrade of a thermal evaporator with a dual MiniE-beam evaporator with focus on the evaporation of platinum. *Instrum. Sci. Technol.* **2006**, *34*(5), 501–507.
7. Sears, F. W.; Salinger, G. L. *Thermodynamics, Kinetic Theory, and Statistical Thermodynamics*; Addison-Wesley Publishing Company, Inc.: Boston, Massachusetts, 1975, 193–195.
8. http://pst4thinfilm.de/index.php?id=31&L=1, Plasma & Semiconductor Technologies GmbH, 2013.
9. Lide, D. R. *Handbook of Chemistry and Physics*; Chemical Rubber Publishing Company, Inc.: Boca Raton, FL, USA, 1990–1991.
10. http://www.alfa.com, Alfa Aesar - Johnson Matthey Company, 2013.
11. http://www.espimetals.com, ESPICorp Inc., 2013.
12. http://www.goodfellow.com, Goodfellow Group of Companies, 2013.
13. Romero, C. P.; Trabol, R. A.; Avila, J. I.; Lievens, P.; Cabrera, A. L. Unexpected large hydrogen adsorption by Nb cluster films under mild conditions of pressure and temperature. *Int. J. Hydrogen Ener.* **2011**, *36*(21), 13595–13602.