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Ion Beam Sputter Deposition of Rare Materials for Thin Films

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Abstract. An instrument for creating 10nm to 10μm+ films of highly enriched isotope for use as nuclear targets has been developed. The main purpose is to maximize target utilization with making thin films of expensive isotopic materials. This instrument is based on the technique called ion beam sputter deposition (IBSD). Typical techniques such as e-beam or thermal evaporation create a very broad plume of evaporated material that coats most of the chamber resulting in large unrecoverable losses. The other main advantage is that the target can be as 10mg or less to allow coating of the substrate and is not limited to any specific geometry as required with other sputter instruments. The instrument is also interfaced with an inert atmosphere glovebox so reactive materials can be made into films and thin sheets onto the substrate of choice. This instrument extends the range of isotope materials available as thin films from Oak Ridge National Laboratory.

Note: Ion beam sputtering deposition terminology refers to the ion beam as the "source", the parent batch of isotope material as the "target" and the resulting film as the "substrate." This differs in the use of these terms from the community that makes "targets" which will be referred to as "nuclear targets" to avoid ambiguity.

Introduction

Enriched stable isotopes are some of the most rare and expensive materials. Researchers have many uses for thin films of enriched isotopes. Isotopes are the fundamental tools for determining nuclear cross sections,[1, 2] nuclear detectors, making medical isotopes[3], diffusion studies[4], calibration sources for analytical methods and determining the transport within such complex systems as ablated particles within fusion plasma reactors[5] or nutrients within the human body.[6] Thin films to foils can be helpful for dispensing sub-milligram quantities using an area and a known thickness instead of measuring by mass.

Despite many advances in technology, the availability of some isotopic nuclear targets has lessened as expertise has retired, older equipment has fallen into disrepair, health/safety regulations have become more restrictive and most capital investments for thin film manufacturing have recently been spent for instruments making highly uniform films for electronics and semiconductor manufacturing. Many nuclear targets that were "easily" obtainable in the 1950s to 1980s are very limited or impossible to obtain in today's market. The advanced electronics grade manufacturing equipment is exceptional for making completely uniform thin films but the efficiency for making small nuclear targets is very low which is both expensive and wasteful of irreplaceable enriched isotopes. The lack of a suitable deposition tool is limiting the ability for some research. Other U.S. national laboratories have similar reduction in capabilities. Internationally, the trend is similar with the lessened ability to prepare high quality isotopic nuclear target materials.

While many techniques exist for making thin films, most of the modern, commercially-available instruments are being optimized for the semiconductor industry which values perfect uniformity and long-lasting production equipment over the cost of materials. Thermal evaporation, sputter deposition, electron beam evaporation and chemical vapor deposition are some of the many methods for materials deposition.[7, 8] For all but a few methods, deposition occurs over most interior walls of the vacuum chamber. Some are specific to only a few elements or compounds. In most cases including "precious metal" deposition, the cost of the labor far exceeds the value of any materials lost to the chamber walls. Precious metals are only pennies per milligram (Au = 3.8¢/mg, Pt = 2.6¢/mg, Rh = 8.3¢/mg).[9] Commercial instruments for deposition of thin films is good enough for industry and many non-enriched natural abundance nuclear targets, but they are not

ideally suited for isotopes due to the low target utilization and need for large size targets.

Isotope deposition inverts the cost structure. Prices can vary from about $1/mg to over $20k/mg for stable isotopes. Synthetic, radioactive, enriched isotopes can greatly exceed this range. For some isotopes, the entire U.S. inventory has been depleted. Many enriched isotopes are not currently produced domestically but may be available from foreign sources. New electromagnetic separation instruments have recently been developed and are used to separate high demand isotopes to higher levels of enrichment. Beyond the economics, conservation of isotope inventory that is not easily replaced is a primary importance in preserving this national asset.

Efficient target utilization requires a deposition plume that is narrowly confined to the receiving substrate. If the deposition is not 100% efficient the method must allow recovery of everything that does not land on the substrate. Recovery of the material deposited within the chamber is complicated by cross contamination with other materials, complex methods needed to recover the isotopes and incomplete recovery. For radioisotopes, the deposition within the chamber cannot be recovered and the entire instrument in addition to the exceedingly rare isotope is disposed of as radioactive hazardous waste. Attempts to recover excess material can become airborne creating further hazards.

Being good stewards of our Department of Energy national resource of enriched isotopes requires near 100% efficient use of the precious material for advancing science.

Ion Beam Sputter Deposition

Oak Ridge National Laboratory has recently invested in developing an ion beam sputter deposition (IBSD) instrument shown in Figure 1 with initial runs to be completed in November 2018. The new IBSD tool was developed to meet the needs of the nuclear target community and other demanding applications. This was designed and built to be a compact, right-sized instrument for making small nuclear targets while minimizing the losses due to deposition upon surfaces other than the desired nuclear target. It is amenable to a wide variety of metals, non-metals, compounds, alloys and semiconductors that can be worked in air or inert atmospheres.

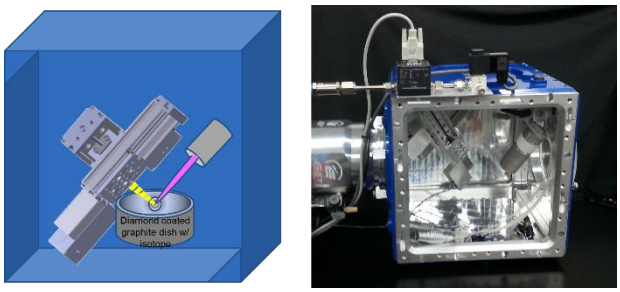

Fig. 1 – Left – Concept drawing of the ion beam sputter deposition instrument with an inert gas ion gun focused on an isotopic source creating a plume of sputtered isotope onto a x-y stage with the substrate to be coated. **Right** – Finished instrument including KRI ion source, Zaber x-y stage, Penta PVD chamber, turbo pump, mass flow controller and quartz crystal microbalance thickness monitor.

IBSD is a technique that generates a plume of sputtered material that can be deposited on a substrate. By

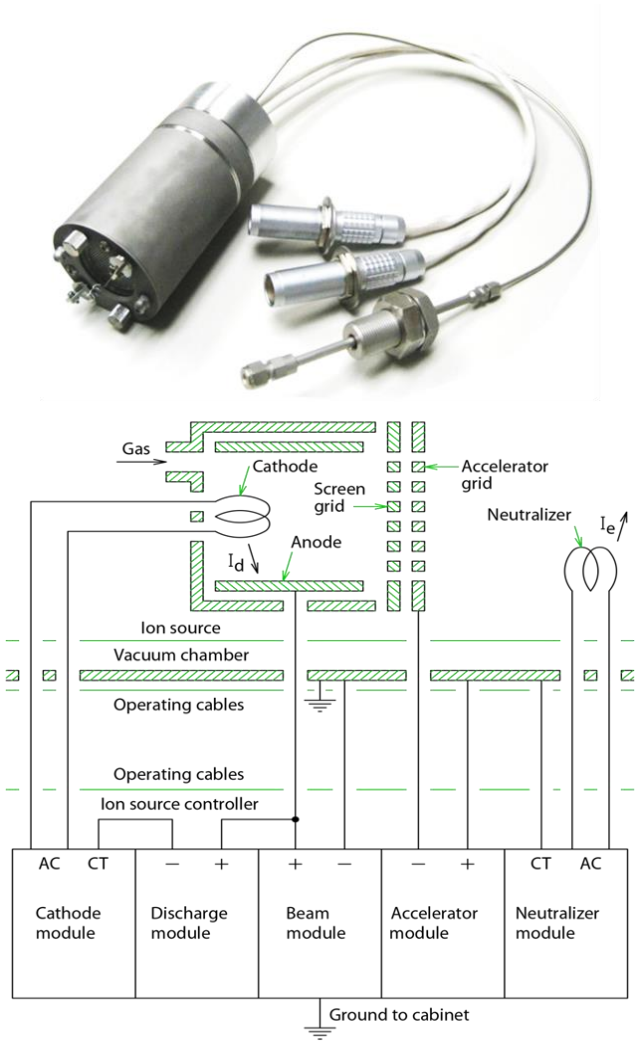

Fig. 2 – Above – Kaufman and Robinson, Inc, Model KDC10 ion source. **Below** – Simplified electrical schematic of KDC10 ion source together with the power supplies necessary to operate this ion source.

choosing the ion mass, energy, and angle of incidence, the directionality of this plume can be optimized such that most of the material gets deposited on the substrate instead of the chamber. The minimal amount of material that does get deposited the surrounding area can be captured on a carbon plate or other substrate for reclamation. Although IBSD is not a new technique, it does not seem to be widely used with isotopes. INTDS Proceedings show the first use with isotopes by Baumann, et. al. in 1979 [10] and nine times since then.[11]

The ion beam is generated with a Kaufman & Robinson, Inc. Model KDC10 ion source (pictured in Figure 2). This is a two grid Kaufman type ion source that ionizes the source gas with electrons from a hot filament then accelerates the ions to energies up to 1000eV. Current densities of ~22mA/cm^2 can be achieved in a focused beam (< 1cm diameter) of 600eV argon ions.

The ideal thin film for most applications would have no other atoms other than the desired target material. The isotope source will generally be in the form of a metal or compound that has been arc melted into a bead, flattened and suspended upon a pedestal and support structure of ATJ nuclear grade graphite platform as shown in Figure 3. Alternatively, the source metal could be a high purity flake of metal that comes directly from the isotope separator. The graphite support is further reduced in cross section to the beam as a pedestal that supports the isotope sputter target. Only the material to be sputtered will present significant surface area to the ion beam. Every material has a different sputtering rate, and graphite is chosen for a support because it has a one of the lowest sputtering yields of any material.

Fig. 3 – Sputter source holder A graphite pedestal supports an 8.9 mg flake of enriched Ru-102.

Sputtering with ion energies below the sputter threshold of carbon can reduce contamination of the deposited films. The rate of sputtering for a given material is dependent not only upon the material itself, but also the mass, energy and angle of incidence of the ions. Generally, sputtering is most effective if the atomic mass of the source gas ions is similar to the target material's atomic mass due to effective momentum transfer.

The threshold for sputtering of carbon using Xe^+ ions impinging at 30° to normal incidence is 323eV.[12] The transition metals range from 9-92eV. Lead has one of the lowest thresholds for Xe^+ ions of just 9eV. As a result, the etch rate for lead is 3200Å/min using a 300eV, 1mA/cm^2 beam with no detectable carbon erosion. While lead is one of the easiest to sputter, silicon has a 92eV threshold. It can still be sputtered by Xe^+ below the threshold for carbon erosion, but the rate is considerably slower at 120Å/min under those same conditions.[12] Even if 600eV ions are used to triple the Si etching rate, the carbon erosion will be about 25X slower than carbon. Table 1 gives other relevant sputtering rates for comparison.

Optimizing the geometry by placing the target material at the focus of the ion beam and minimizing the area of the graphite pedestal exposed to the beam will ensure negligible carbon contamination in the final coating. The purity of the target material will be the primary source of impurity atoms that get deposited onto the substrate.

Table 1 – Sputter threshold and etch rates for various elements using Xe^+ ions as determined by Seah (2005).

Material	Threshold (eV)	Etch rate at 300 eV ion energy (Å/min)	Etch rate at 1200 eV ion energy (Å/min)
Si	92	120	800
Ti	61	180	840
Ru	47	290	1100
Y	33	500	1700
Nd	18	1400	3800
Pb	9	3200	7800
C	323	0	96

The incident ion beam striking upon the target results in emission of sputtered particles. Lautenschläger, et al [13] showed that angular distribution of sputtered atoms has a strong dependence upon the ion mass, energy and angle of incidence. The total contribution can be separated into isotropic and anisotropic components. Figure 4a shows the particle flux distribution resulting

from low energy (500eV incident ions). The Ar^+ ion beam at -30° from normal can effectively transfer forward momentum to the target atoms with a roughly gaussian distribution centered at +50°. In contrast, Figure 4b show the sputtered particle flux distribution at 1.5keV. While a similar number of particles gain forward momentum from the source ion beam, the additional beam energy does sputter more particles, the extra energy penetrates below the surface resulting in collisional cascades that transfer momentum omnidirectionally within the target. The isotropic contribution to the total sputtered plume greatly exceeds the desired anisotropic contribution. At these higher energies the narrow plume is lost.

The substrate to be coated will be mounted to a computer-controlled x-y linear stage positioned at an optimal angle and rastered to collect a uniform coating of sputtered isotope material. The substrate can

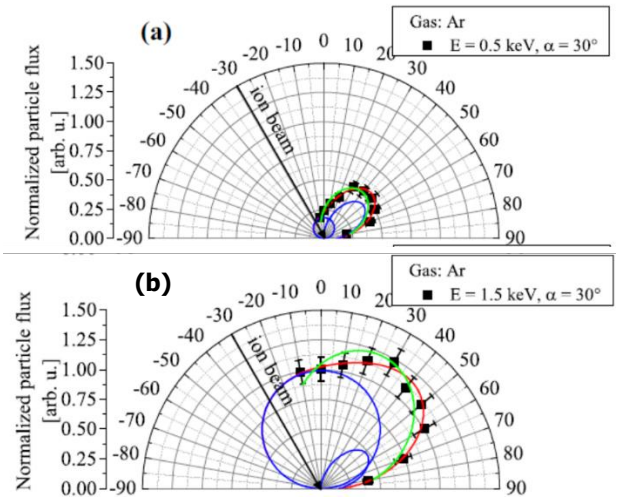

Fig. 4 – Study of ion beam sputtering of polycrystalline titanium by Lautenschläger et al. with an incident Ar ion beam 30° at energy of **(a)** 500ev and **(b)** 1.5keV. As the energy is increased the overall plume of sputtered particles becomes broader and less directional. (Reprinted by permission of Elsevier License 4441910728316)

be a supporting film such as standard carbon foils, aluminum or polymer, or the support can be sacrificial so removal results in a freestanding film if sufficiently thick to be self-supporting.

The interface between the chamber and glove box is a critical design feature of this instrument. The chamber is a modular Penta-PVD, 30cm cube vacuum chamber made from 6061 aluminum alloy as shown in Figure 5. It includes a scroll pump station backing a turbomolecular pump with a base pressure $2x10^{-7}$ Torr. A front door can be used for setup or when working with air stable materials. A side door allows direct

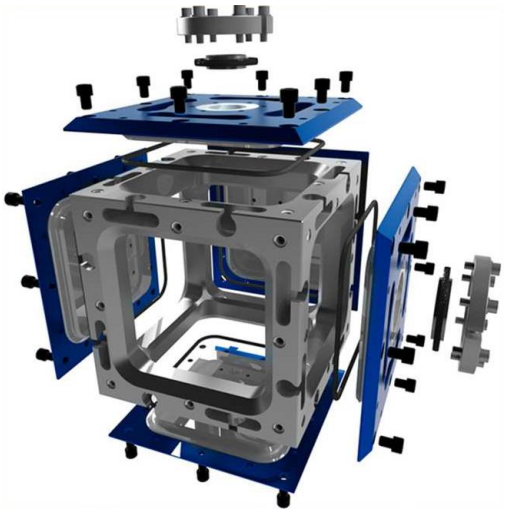

Fig. 5 – Penta-PVD Chamber The chamber is a modular system that can be reconfigured if the needs change.

passage into an inert atmosphere glove box. This dual-entry chamber can allow the chamber to function as an additional antechamber for the glove box. The interface with the glovebox allows highly reactive isotopes such as lithium, calcium, strontium or barium to be handled entirely within an air-free, moisture-free environment.

Process monitoring will be done by intermittent insertion of a quartz crystal microbalance into the sputtered beam. A programmable logic controller will assist in automation of the deposition for reproducibility between runs. The system includes Underwriter Laboratory compliance with lock-out/tag-out capabilities built in. The design of this instrument has been a collaboration between Oak Ridge National Laboratory, Kaufman & Robinson, Inc. and AGS Plasma Systems, Inc.

Conclusion

An instrument dedicated to the ion beam sputter deposition of isotopes has been created and is awaiting installation at Oak Ridge National Laboratory. The deposition of rare materials that would not otherwise be considered due to the inevitable losses that occur with most deposition methods will be enabled. Furthermore, the interface to an inert atmosphere glove box will allow for sputtering of reactive metals such as the alkali, alkaline earths, early transition metals, rare earths and metalloids from which oxide free thin films are otherwise challenging to produce. In the future, the range of materials will include the naturally occurring radioactive enriched isotopes and transuranic isotopes.

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