JVSTA Journal of Vacuum Science & Technology A

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Citation: Journal of Vacuum Science & Technology A **14**, 2677 (1996); doi: 10.1116/1.580185
View online: http://dx.doi.org/10.1116/1.580185
View Table of Contents: http://scitation.aip.org/content/avs/journal/jvsta/14/4?ver=pdfcov
Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

Cheap and stable titanium source for use in oxide molecular beam epitaxy systems

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(Received 22 December 1995; accepted 12 April 1996)

The emergence of molecular beam epitaxy (MBE) as an unparalleled technique for growing high quality epitaxial oxides, oxide heterostructures, and layered oxide superlattices[1–3] has generated a need for stable effusion cell sources for low vapor pressure solids.[4] Titanium poses a particular problem because of the high temperatures required (>1500 °C) to achieve an acceptable sublimation rate. The family of titanates includes insulators, ferroelectrics, antiferroelectrics, and even superconductors. The ability to fabricate titanates provides the MBE researcher with an arsenal of additional perovskites that are structurally matched to other perovskites actively being researched by MBE, e.g., the well known cuprate superconductor phases. Recently, several groups have reported the growth of titanates by physical vapor deposition using electron-beam (*e*-beam) evaporation[5,6] or high-temperature effusion cells.[3] Using a high-temperature effusion cell for titanium, Eckstein *et al.* report stabilities in atomic flux of a few percent over periods of hours for all of their sources.[3] Commercially available high-temperature cells have several drawbacks, including high cost, relatively small crucible volume, and the difficulty in finding a suitable crucible material. Similarly, *e*-beam sources are expensive and achieving flux stability of a few percent over periods of hours is difficult.

Our solution employs a titanium sublimation pump known as a Ti-Ball™ (Ref. 7). It is used traditionally as an aid to vacuum pumping where titanium is a ''getter'' atom to which colliding reactive gases have a high sticking coefficient. The Ti-Ball™ consists of a hollow prolate spheroid of titanium (~35 g of usable titanium) encasing a coiled tungsten filament.[8,9] The filament is crimped on the top and bottom to a molybdenum nipple and support leg, respectively.[8,9] The spheroid itself is supported by four molybdenum wires which are in turn spot welded to an insulated stainless steel base.[8,9] Power is supplied from an external power supply, which in our case was a stable dc supply for source flux stability. The bulk of the resistive load is carried by the tungsten filament which radiatively heats the titanium internally and provides a uniform temperature distribution through the ball. The Ti-Ball™ is designed for a maximum operating temperature of approximately 1600 °C at 750 W.[8,9]

In their description of the development of the Ti-Ball™, Hara and Snouse[9] reported the sublimation rate of a Ti-Ball™ over a period of more than 80 h. They demonstrated a sublimation rate of ~0.5 g/h ±30% over the first 70 h of operation.[9] We wondered if a Ti-Ball™, heated with a stable power supply, could be used as a stable titanium source for thin film deposition over periods of several hours. Here we report our analysis of the stability of the titanium deposition rate, the effect of ozone gas on this stability, and the purity of the deposited films.

Our setup consists of a Ti-Ball™ source powered by an HP 6268A dc power supply. The Ti-Ball™ is mounted in a water-cooled stainless steel enclosure (with a nominal inner diameter of 4.8 cm) typically used for MBE effusion cells.[10] The inner wall of the cooling jacket is lined with coiled sheets of titanium metal 0.25 mm thick. This foil prevents deposited titanium from peeling off of the walls of the water cooling jacket and thermally shorting the Ti-Ball™ to the water-cooled enclosure. Oxidant is supplied to the chamber in the form of purified ozone. Ozone is first made by flowing oxygen through a PCI Ozone Corporation model G1-L generator. The ozone is then purified in an ozone distillation apparatus previously described by Schlom and Harris.[2] All deposition thicknesses are measured with an Inficon IC 6000 quartz crystal monitor. The water-cooled quartz crystal is located 20.6 cm from the center of mass of the titanium spheroid. The thickness is recorded automatically by computer as a function of time. The deposition rates are calculated from this data over time intervals such that the error bars of the deposition rate (due to the finite (1 Å) resolution of the quartz crystal monitor) are comparable to the long term stability of the deposition rate. All depositions were performed with an output power of ~700 W to the Ti-Ball.™ This choice of power gave us approximately 50 h of stable output from the Ti-Ball™ while maintaining acceptable titanium deposition rates. The Ti-Balls™ used in these experiments were outgassed to remove the adsorbed contaminants from the surface in accordance with the recommendations of the manufacturer.

One of the major pitfalls in the MBE growth of oxides is the formation of oxides on the source materials, which can result in large changes in the source flux despite the stability of the effusion cell temperature. The oxidation of alkaline earth source materials in effusion cells following the introduction of an oxidant has been well documented by Hellman and Hartford.[11] In the case of Mg, Ca, and Sr sources, they found the flux to decrease exponentially with increasing oxygen pressure.[11] In contrast, the Ba flux increased linearly with O_2 pressure.[11] Similarly, studies have been done by Kuznetsov, Nasarov, and Ivanovsky[12] on the sublimation rate of titanium in various N_2 and CO ambients. They found that at lower sublimation temperatures (1300–1350 °C) the tita-

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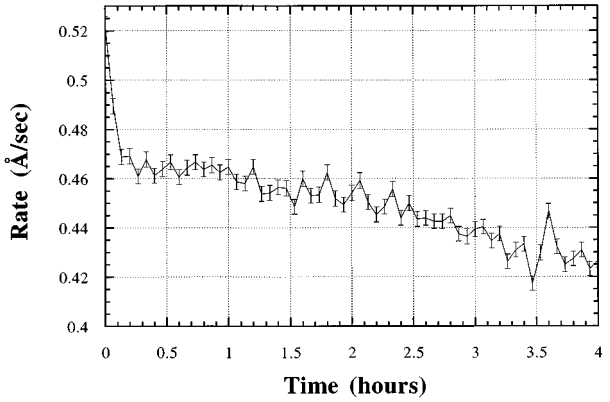

FIG. 1. Titanium dioxide deposition rate (Å/s) vs time (hours) deposited in a background ozone pressure of 5.0×10^{-5} Torr. An input power of 700 W to the Ti-Ball™ was used.

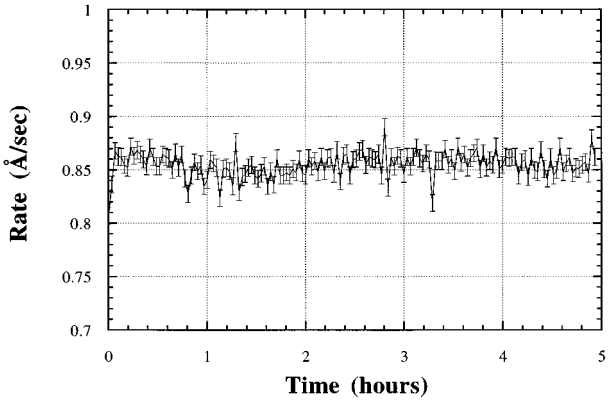

FIG. 2. Titanium dioxide deposition rate (Å/s) vs time (hours) deposited in a background ozone pressure of 2.0×10^{-6} Torr. An input power of 700 W to the Ti-Ball™ was used.

nium sublimation rate decreased and finally stopped as the background pressures were increased.

In addition to the potential effect of an oxidizing gas on the stability of the evaporating titanium flux from a Ti-Ball,™ we were concerned about the introduction of impurities into the depositing flux due to the oxidation of the hot molybdenum components of the Ti-Ball.™ MoO_3 is known to be extremely volatile at high temperatures.[13] Numerous researchers utilizing MBE to grow oxides have seen molybdenum contaminants in their films that resulted from using hot molybdenum parts in an oxidizing environment.[2] In the case of the Ti-Ball™ the molybdenum nipple and support legs are a source of concern. In case this turned out to be a problem, we fabricated a Ti-Ball™ in which all the molybdenum parts within line of site of the substrate were replaced by hafnium parts. Unlike molybdenum, hafnium *and* its oxides are extremely refractory. As it was realized that the titanium flux would lower the ozone partial pressure in the vicinity of the Ti-Ball,™ perhaps sufficiently to protect the molybdenum parts, the Ti-Ball™ was always heated and cooled under vacuum conditions.[14]

Figure 1 shows the deposition rate of TiO_2 in Å/s over a 4.5 h period in an ozone pressure of 5.0×10^{-5} Torr. The deposition rate decreases by ~2.5% per hour. A patchy oxide scale was seen on the Ti-Ball™ surface (after cooling in vacuum) following growth at these conditions. The decrease in flux is attributed to the formation of this oxide scale on the Ti-Ball.™ Figure 2 shows the same Ti-Ball subject to an ozone background pressure of 2.0×10^{-6} Torr. The deposition rate remains fairly constant with fluctuations of approximately $\pm2.5\%$ over a period of 5 h. Similarly, Fig. 3 shows the deposition of titanium in vacuum with a stability roughly $\pm2.0\%$ over a period of 4 h. All data shown are with an input power of ~700 W to the Ti-Ball™, and have a starting base pressure of 1.0×10^{-7} Torr. The warmup period of 30–40 min is not shown in each graph.

The purity of the deposited TiO_2 films was analyzed by electron microprobe analysis (EMPA) and direct current plasma emission spectrometry (DCP) on films deposited in both 5.0×10^{-5} and 2.0×10^{-6} Torr of ozone. Results indicated no molybdenum contamination down to the detection limit of 1000 ppm (0.1%) by EPMA, and 100 ppm (0.01%) by DCP.

The Ti-Ball™ source has proven to be a stable source of titanium for thin film depositions in oxide MBE systems with a stability as good or better than that of conventional high-temperature effusion cells. We were able to achieve a stable titanium flux ($\pm2\%$ in vacuum) over a 4.5 h period simply by using a stable power supply (i.e., without rate-monitor feedback). Similar stabilities ($\pm2.5\%$) were seen using a low background pressure of 2.0×10^{-6} Torr of ozone. No molybdenum contamination in films deposited at a background pressure as high as 5.0×10^{-5} Torr of ozone was detected by EMPA or DCP. The cost of a Ti-Ball™ with a holder is more than an order of magnitude less than a high-temperature effusion cell or *e*-beam source. Replacement Ti-Balls™ are about the same price as replacement crucibles. Thus, the Ti-Ball™ is a cheap and stable source of titanium for most oxide MBE applications.

Acknowledgments: The authors would like to thank Varian Associates, and EPI for help in the fabrication of a

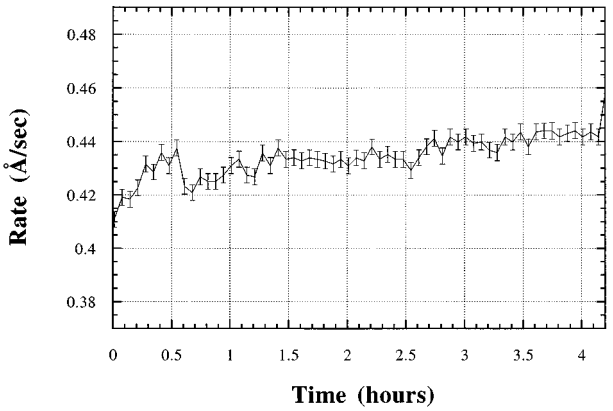

FIG. 3. Titanium metal deposition rate (Å/s) vs time (hours) deposited in vacuum with a 1.0×10^{-7} Torr base pressure. An input power of 700 W to the Ti-Ball™ was used.

hafnium substituted Ti-Ball.™ The authors gratefully acknowledge the financial support of the NSF through Contracts Nos. DMR-9312072 and DMR-9357614.

[1]R. A. McKee, F. J. Walker, E. D. Specht, G. E. Jellison, Jr., and L. A. Boatner, Phys. Rev. Lett. **72**, 2741 (1994).
[2]D. G. Schlom and J. S. Harris Jr., in *Molecular Beam Epitaxy: Applications to Key Materials*, edited by R. F. C. Farrow (Noyes, Park Ridge, 1995), pp. 505–622.
[3]J. N. Eckstein, I. Bozovic, and G. G. Virshup, MRS Bull. **19**, 44 (1994).
[4]E. Coleman, T. Siegrist, and J. J. Yeh, J. Electron. Mater. **19**, 235 (1990).
[5]K. Iijima, T. Terashima, K. Yamamoto, K. Hirata, and Y. Bando, Appl. Phys. Lett. **56**, 527 (1990).
[6]H. Nozoye, N. Nishimiya, and H. Sato, Appl. Phys. Lett. **54**, 231 (1989).
[7]Ti-Ball™ is a registered trademark of Varian Associates, Vacuum Products Division, Lexington, MA.
[8]K. M. Welch, *Capture Pumping Technology, An Introduction*, 1st ed. (Pergamon, New York, 1991), pp. 210–212.
[9]D. J. Harra and T. W. Snouse, J. Vac. Sci. Technol. **9**, 552 (1971).
[10]EPI, Chorus Corporation, St. Paul, MN.
[11]E. S. Hellman and E. H. Hartford, Jr., J. Vac. Sci. Technol. B **12**, 1778 (1994).
[12]M. V. Kuznetsov, A. S. Nasarov, and G. F. Ivanovsky, J. Vac. Sci. Technol. **6**, 34 (1969).
[13]*The Oxide Handbook*, 2nd ed., edited by G. V. Samsonov (IFI Plenum, New York, 1982), p. 153.
[14]When thermally cycling the Ti-Ball™, it is important to cool or heat slowly through the titanium $\alpha \rightarrow \beta$ transition which occurs in pure titanium at ~880 °C (Refs. 8 and 9). It is recommended that the Ti-Ball™ be kept above ~200 W when not in use (Ref. 8). At this power the titanium sublimation rate is negligible, but the temperature remains above the transition point (Ref. 8). Rapid thermal cycling causes the surface to roughen and increases the net surface area. This increased surface area can result in a significant decrease in the titanium sublimation rate (Ref. 8).