A Novel Method for TiN Thin Film Deposition for Next-Generation Electron Source Photocathodes

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Abstract

Titanium Nitride (TiN) has recently garnered much interest as a potential photocathodic material with superior properties to conventional materials [1] and as a protective thin film for air-sensitive photocathode materials. TiN thin films can be grown on various substrates using magnetron sputtering or vapour deposition techniques. However, these require an existing sputter target or powder of high-quality TiN. This study presents a molecular beam epitaxy approach to TiN thin film growth, developing a method of TiN deposition via reactive ion beam sputtering. Ti and TiN thin films were grown on Cu, SiO_2 and Si substrates and are characterised using AFM, XPS and low magnification light microscopy. The geometry of the deposition chamber and its effect on uniformity and quality of the growth product is also discussed. XPS analysis confirms the presence of TiN on the surface via the shifted N 1s peak.

Introduction

Electron sources are a vital constituent in many modern technologies, both in research and in commercial applications[1]. In accelerator applications, electron source photocathodes are a key component of the photoinjector, which replaced the thermionic electron source in 1983, providing a drastic improvement in beam brightness [2]. Unfortunately, some of the most promising materials for future high-performance photocathodes prove to be extremely vulnerable to atmospheric poisoning, as well as rapid degradation by the high electric field strength and high-power drive laser [3].

Metal and metal oxide photocathodes exhibit a greater resistance to degradation than semiconductor or other air-sensitive photocathode materials, however metals also tend to exhibit a lower quantum efficiency (QE) , sacrificing performance for longevity. The aim of this study is to combine the advantages of both air-sensitive semiconductors and alkali metals with higher QE, and more robust metals and metal oxides whilst also keeping the process of manufacture as simple as possible.

We aim to produce a chemically and physically robust thin-film over the air-sensitive photocathode material. The material of interest to this study is titanium nitride. As a high hardness and strongly bonded ceramic material, TiN thin-films are an excellent choice of material to increase the lifetime of Cu photocathodes [4]. With a work function of **4.3 – 4.65** eV it also lies very close to Cu (at **4.6**) allowing effective illumination in the UV range, reducing dark current [5].

The deposition of TiN via reactive magnetron sputtering is well established in the field, however we hope that using a more MBE style method it will be possible to produce highly crystalline thin-films which interfere minimally with the optimised properties of the photocathodic layer beneath.

Deposition Method

Titanium is deposited using a hot Ti filament (adapted from a titanium sublimation pump cartridge). The Ti condenses on a cold (300K) substrate approximately 10cm away.
N_2 gas is ionised using an AG2 ion gun and the resulting ion beam is accelerated towards the target substrate. It is unclear at this time what proportion (if any) of the N≡N bonds are broken in the AG2 plasma.

Incident N* (likely N_2^+) on the Ti surface are either implanted or serve to remove material as in conventional sputter cleaning, resulting in a much slower and more controllable growth rate.

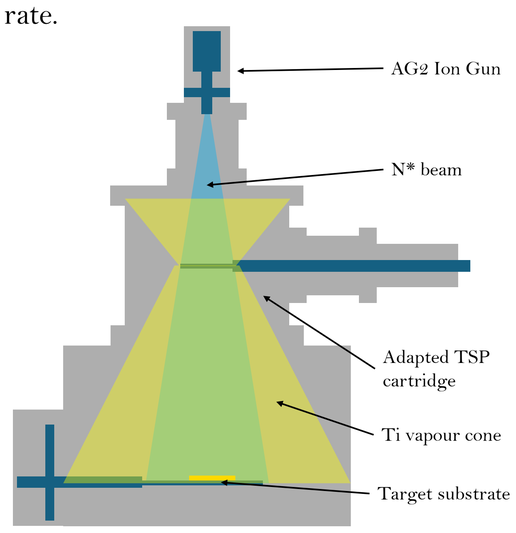

Figure 1: A schematic of the deposition setup. The geometry of the beam and vapour cone is critical for uniform deposition across the substrate. The two components are designed to impinge on the sample co-axially.

Left: A custom beam guide attached to an AG2 ion gun. The guide is lined with Ti and protects the internals of the ion gun from the majority of the Ti vapour.
Right: The Ti filament with attached Ti foil shield. This protects the filament from the ion beam during deposition.

Left: The ion beam passing through the loop filament. Under these conditions, the top of the filament is affected by the beam, causing uneven heating and eventual filament failure as shown right. This is mitigated with the Ti foil shield shown above.

Initial XPS

XPS was performed on a Cu substrate sample before and after growth of a thin film.
The addition of both the Ti 2p and N 1s peaks after growth confirm the presence of both Ti and N on the sample.
The N 1s peak is also shifted by ~2eV (lower BE) indicating Ti-N bonding is present.

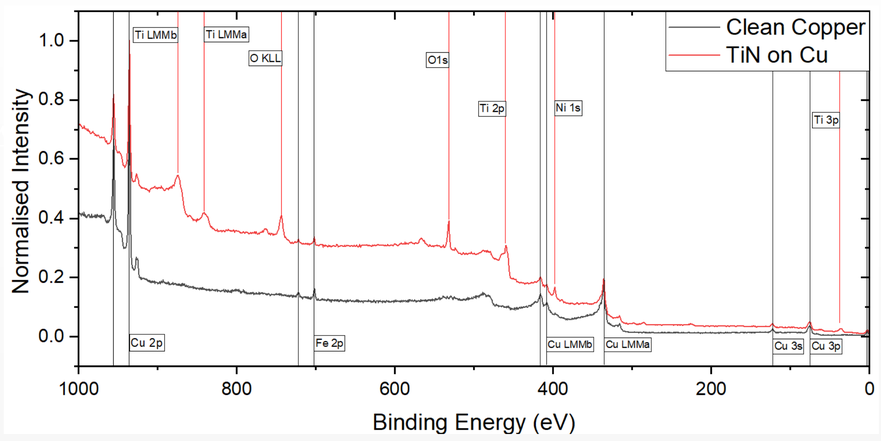

Fig 3. The XPS spectra of both a clean polished Cu sample and a thin TiN film grown on the same sample. Black vertical lines show shared peaks between the spectra, while red vertical lines show the new peaks detected after growth of the TiN thin film.

Further Analysis

Titanium nitride films were deposited onto a number of substrates including polished Cu and Ag, as well as semiconducting GaAs and Si. Initially a deposition rate was calibrated using films of different thicknesses.

Figure 4: Shows a series of TiN films deposited on polished Ag for different times. From left to right, 3hrs, 2hrs, 1hr, 45 mins 30mins, 15mins, control.

Although too rough for AFM, XPS of these samples showed strong Ti and N peak contributions, with the substrate peaks clearly diminishing in intensity as film thickness increased. It is inferred from these results that the composition of the film is uniform throughout its thickness, even at higher thicknesses.

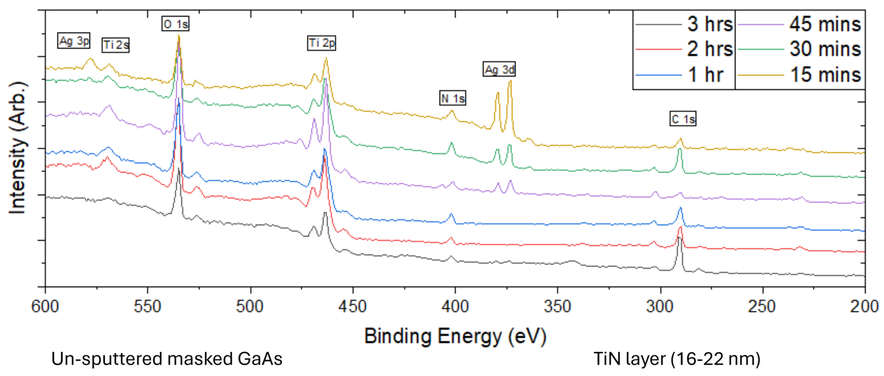

Figure 5: XPS survey spectra for the samples shown in figure 4. The intensity of the Ag 3d structure clearly indicates the increasing thickness of the TiN overlayer. The spectra are normalised and offset for clarity of presentation.

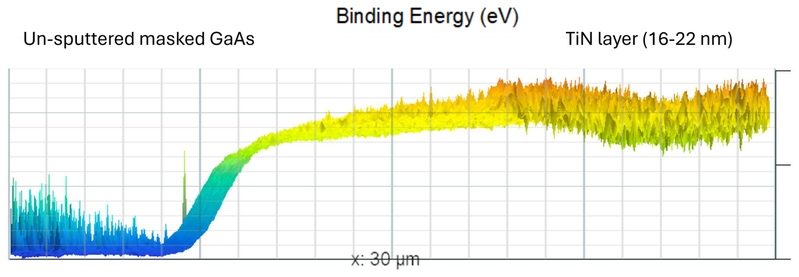

Figure 6: Shows a side view of a 3D reconstruction of a typical section of the edge of a TiN film using AFM. There is considerable variation across this step which can be seen on the light micrograph in figure 7. This variation settles out very quickly however away from the edge of the film.

The produced films are formed of mainly TiN with some evidence of TiC and TiO present as well, although it is difficult to confirm the stoichiometry of the films due to surface contamination from air transfers into the analysis chamber.

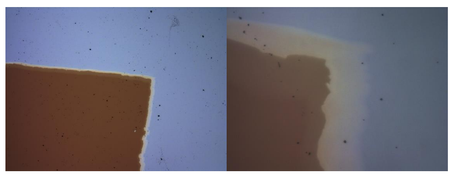

Figure 7: An optical micrograph of the corner of one of the TiN films on GaAs substrate at 10x (left) and 100x (right) magnification. The area around the edge of the film shows three distinct bands ranging in colour from dark to light. These three bands can be attributed to differences in thickness seen in figure 6, but may also differ in chemical composition.

Conclusions

- Owing to favourable properties such as high mechanical and chemical resistance and a similar work function to existing photocathode materials such as Cu, TiN was investigated as a protective overlayer to improve the lifetime of photoinjector photocathodes.
- A novel method was investigated which requires only a Ti wire filament and clean N_2 gas.
- This method was shown to be successful at producing TiN thin films with some TiO and TiC formed as well (likely during sample transport between growth chamber and the XPS facility).
- The geometry of the growth system was found to have a significant effect on the homogeneity and uniformity of the films formed using this method. Owing to the topological differences in the samples and sample holders, clear discontinuities between dissimilar materials were formed and were identified visually using light microscopy.
- The film growth rate was investigated on various substrates using AFM and was found to be linear in time but heavily dependent on the system geometry. For our system we calibrated the growth rate at ~20nm per hour.
- The edges of the masked area were found to have interesting variation in thickness and possibly composition.

Future Work

- Image XPS could be used to further characterise the distribution of materials on films, as well as to non-uniformity of the region near step-edges. It would also be interesting to investigate the chemical uniformity of films away from the edge region.
- Film growth rate is dependant on three immediate factors: Ti filament temperature controlling Ti deposition rate, and the N* beam pressure and beam energy control both the rate of N* implantation as well as the sputter rate. These parameters must be investigated more thoroughly in order to optimise the thin film growth and ensure maximum nitridation of each Ti atomic layer, preventing latent TiO and TiC formation.

References

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