

# Microstructure of Ti Thin Films Formed by Energetic PVD Processes

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Plasma technology is a key technology in most modern industries. Especially physical vapour deposition (PVD) is omnipresent from semiconductor processing to medical devices, tool industry and thin film solar cells, with an estimated market volume of 7 billion USD in 2008 and an annual growth rate beyond 10%. By introducing kinetic ion energy into the surface of a growing film, it is possible to reduce the substrate temperature while maintaining the film morphology. Thus, a dense, columnar structure can be obtained at temperatures of less than 15% of the melting temperature  $T_m$  or an epitaxial single-crystal growth at 50-75% of  $T_m$ . However, the morphology itself in the former case may not be the only desired film quality, texture or electronic properties are also changing with ion energy and substrate temperature. Especially the partition of the energy deposition into activated surface mobility and bulk defects, depending on the ion range, has to be mentioned here. At the same time, the transient local heating during the collision cascades complicates any attempt at calculating an effective surface temperature for diffusion or annealing processes. In this contribution, columnar titanium thin films are produced by ion beam sputtering (IBS) and vacuum arc deposition (VAD) with a similar average energy and a similar film thickness. Similarities and dissimilarities between these films and compared to bulk Ti are highlighted by subsequent oxygen ion implantation (II, 15 keV,  $2 \cdot 10^{18}$  oxygen atoms/cm<sup>2</sup>) at elevated temperatures between 300 and 500°C, and the concomitant investigation of diffusion behaviour [1].

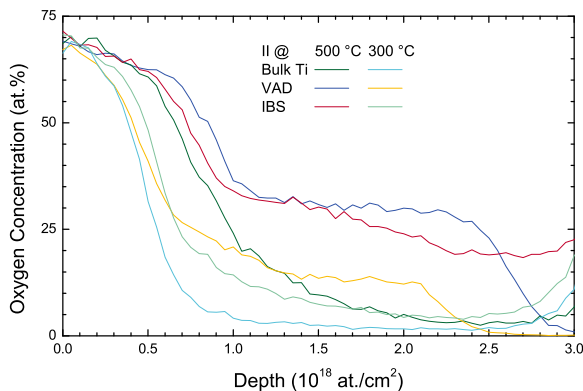


Fig. 1: Oxygen depth profiles as measured with ERDA for selected thin films.

After oxygen II, a closed oxide layer was observed with the thickness always larger than the ion range (and smaller than the total film thickness). The oxygen/titanium ratio in this layer is always 2:1. For bulk samples, a thermally activated diffusion with an activation energy of 0.83 eV is well-known [2]. For thin films, this closed TiO<sub>2</sub> layer has always the same or a larger thickness than for the bulk ma-

terial (see Figs. 1&2). In addition, deep oxygen diffusion tails are observed for the thin films. Straightforward quantification of ERDA results allows a direct presentation of the oxygen content (with selected spectra displayed in Fig. 1). This enhanced oxygen content in the whole thin film is more pronounced for VAD than for IBS, with increasing temperature during ion implantation partially masking the differences. For IBS thin films, additional oxygen enrichment at the interface is present at 450°C and beyond, which is more easily detected using SIMS due to the restricted detection depth range of ERDA.

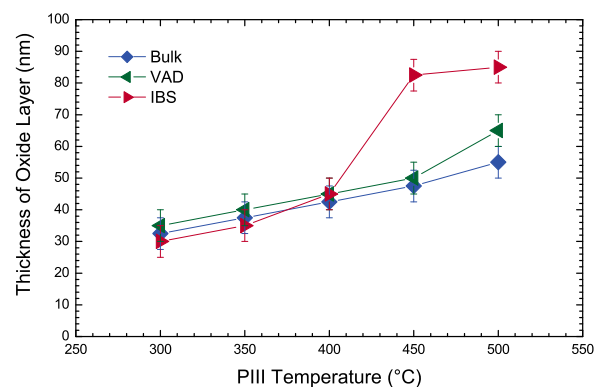


Fig. 2: Thickness of the closed surface TiO<sub>2</sub> layer formed after oxygen PIII as a function of the PIII process temperature.

The presented results can be explained by assuming a distinction between diffusion along grain boundaries and within grains. Correspondingly, differences in the diffusion behaviour and the reactivity for the three Ti substrates can be explained along this line of reasoning. The fraction of grain boundaries is much larger for the thin films than for the bulk material with a grain size of a few micrometer. Thus faster diffusion of oxygen along the grain boundaries can occur in all materials, with the resulting deep oxygen concentration depending on the diffusivity and the grain boundary area density. The higher average energy flux during VAD compared to IBS indicates that the deep oxygen diffusion correlates with the average particle energy, i.e. it represents a direct indicator for the grain boundary density. In contrast, the growth of the surface oxide layer is more closely related with the maximum particle energy, indicating that intragrain defects created by radiation damage are responsible for these nucleation and growth processes.

## References

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