Nucleation and growth of anatase and rutile phase in TiO_2 layers deposited by reactive pulse magnetron sputtering

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Crystalline titanium dioxide films are the subject of scientific studies because of their photocatalytic properties. By irradiation with photon energy higher as the band gap of the crystalline phases electron hole pairs are generated. The photogenerated holes exhibit a strong oxidizing power and can decompose organic pollutants by photocatalysis. Simultaneously the layer surface shows a photo-induced superhydrophilicity. Photocatalytic decomposition and superhydrophilicity of thin TiO_2 films are used for development of new products properties like self cleaning windows, antifogging mirrors, antibacterial tiles, air cleaning and water purification devices [1-4]. The occurring TiO_2 phases, lattice defects and morphology of the films significantly influence the photocatalytic properties [5].

The aim of the present work was the investigation of the effect of pulse mode during reactive pulse magnetron sputtering on nucleation and growth of crystalline TiO_2 phases. By the choice of the pulse mode the amount of energetic particle bombardment of the growing layer is drastically changed. The layers were deposited on silicon wafers without additional substrate heating. The increase of substrate temperature during deposition was below 200 °C.

In the unipolar pulse mode with relative low ion bombardment of the substrate the layer growth starts with the deposition of an amorphous layer. The nucleation of first columnar anatase crystallites can be recognized at a distance of approximately 200 nm. A whole crystalline layer can not be observed until a layer thickness of about 800 nm was reached (Figure 1). The morphology of the films is characterized by well-shaped crystallites with lateral dimensions between 100 and 200 nm.

In contrast in the bipolar pulse mode with drastically higher ion bombardment of the substrate the crystallization of the rutile phase is favoured. At a distance between 100 and 300 nm separated rutile crystallites nucleate in the first deposited amorphous layer. By a pronounced lateral growth of the individual crystallites cone-shaped grains are developed with further film growth. Above a distance of 300 nm from the substrate the layer is completely crystalline. The rutile crystallites have a lateral dimension of about 100 nm at layer surface and are further characterized by a high density of lattice defects without a pronounced crystallite morphology at layer surface (Figure 2).

The occurring phases and their microstructure have a strong influence on the photocatalytic properties of TiO_2 films. Layers with predominately rutile phase and high defect density have a low photocatalytic activity. For good photocatalytic properties the presence of the anatase phase is necessary. Partially crystalline thin layers with amorphous and anatase phases exhibit already excellent superhydrophilic properties but a relative low photocatalytic activity for decomposition of organic substances. This can be probably explained by a high recombination rate of photogenerated electron-hole pairs in amorphous titanium dioxide. A drastic enhancement of photocatalytic decomposition can be observed for thicker layers which consist completely of anatase phase near the layer surface. The results

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have shown that the detailed microscopic investigation of the microstructure development in growth direction enables a better understanding and the basis for further optimization of photocatalytic properties of TiO_2 films.

References

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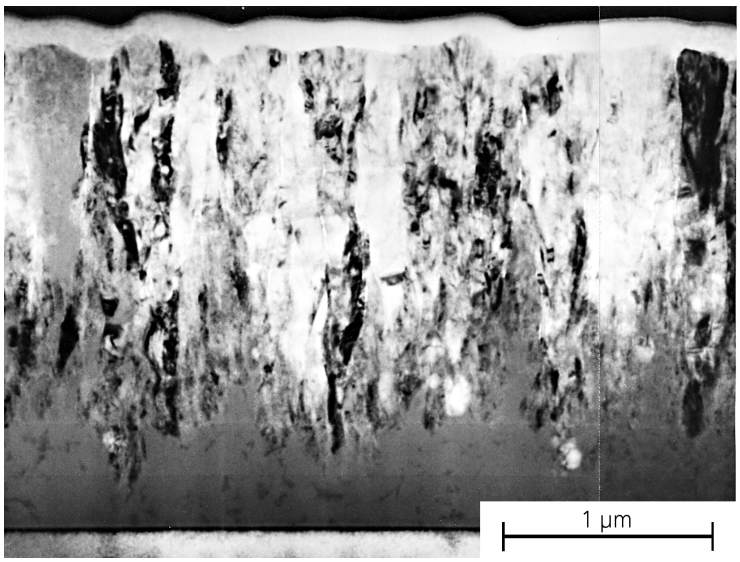

Figure 1. Cross-Section TEM bright field image of a TiO_2 layer with amorphous and anatase phase deposited by pulse magnetron sputtering in unipolar pulse mode.

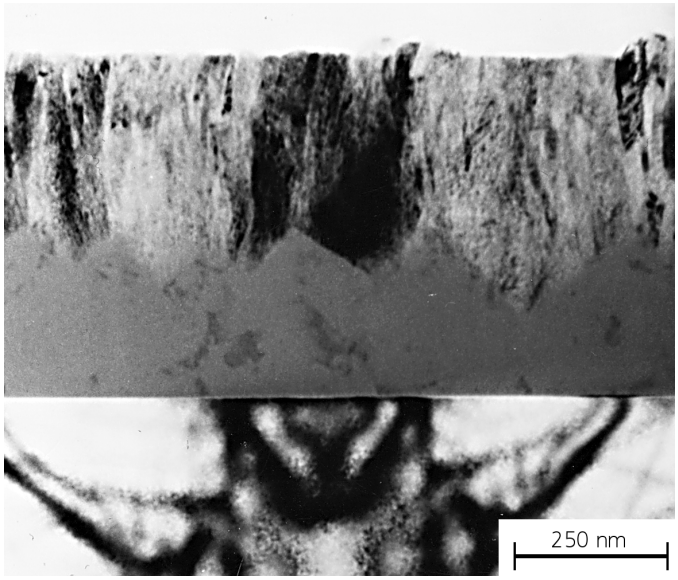

Figure 2. Cross-Section TEM bright field image of a TiO_2 layer with amorphous and rutile phase deposited by pulse magnetron sputtering in bipolar pulse mode.

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