

Deposition and Modification of Semiconductor Thin Films Through Atmospheric Pressure Plasma

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Nanoparticles grown in a plasma are used to visualize the process of film deposition in a pulsed radio-frequency (rf) atmospheric pressure glow discharge. Modulating the plasma makes it possible to successfully prepare porous TiO₂ films^[1]. We study the trapping of the particles in the sheath during the plasma-on phase and compare it with numerical simulations. During the plasma-off phase, the particles are driven to the substrate by the electric field generated by residual ions, leading to the formation of porous TiO₂ film. Using video microscopy, the collective dynamics of particles in the whole process is revealed at the most fundamental "kinetic" level.

Using pulse-modulated atmospheric pressure radio frequency (RF) plasma, dense anatase TiO₂ thin films were successfully deposited on a temperature-sensitive substrate (polyethylene terephthalate)^[2]. Transmission electron microscopy (TEM) results revealed that TiO₂ nanoparticles grown and turn to anatase through plasma in just about 70 ms. Laser light scattering analysis indicated that the TiO₂ particles were trapped above the substrate at a height of approximately 0.27 mm during the plasma process, which is consistent with the simulated plasma sheath thickness of 0.26 mm. A

pulse-modulated atmospheric pressure RF plasma deposition has been proposed.

To enhance the visible light response of TiO₂ films, atmospheric pressure He/H₂ plasma treatment was applied. The originally white TiO₂ thin film turned completely black after plasma modification. The modified thin film exhibited a significant enhancement in visible light absorption and reduction in bandgap, which are advantageous for improving the utilization efficiency of solar radiation. X-ray photoelectron spectroscopy (XPS) results showed that a portion of Ti⁴⁺ had been reduced to Ti³⁺, resulting in self-doping and changes in the band structure. I-V tests indicated that the resistance of the treated samples was reduced by a factor of 10⁷ times compared to the original sample. Hydrogen ions gain high kinetic energy as they are accelerated by the plasma sheath, which is believed to play a crucial role in plasma modification.

References

- [1] Y. Xu et al, arXiv e-prints. 2019, arXiv:1903.09379.
[2] Y. Xu et al, Plasma Process. Polym. **18(10)** 2100050 (2021).

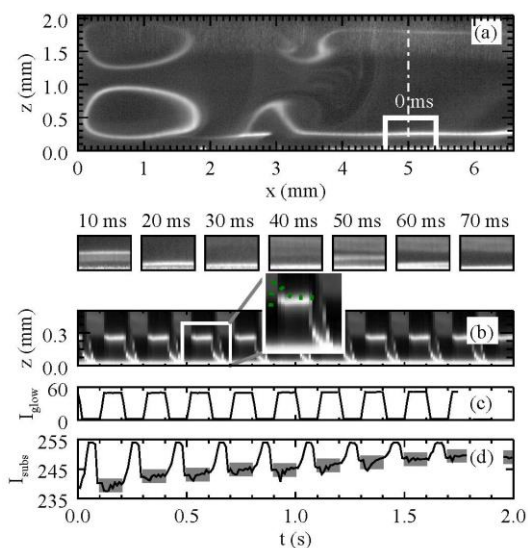


Figure 1. Dust dynamics in plasma, (a) dust distribution from front side view at plasma on time in 50% duty cycle plasma discharge, and (b) dust particles dynamics in the duty cycle discharge, and (c) plasma discharge intensity at the corresponding time to the particles dynamics, and (d) substrate intensity at the corresponding time.

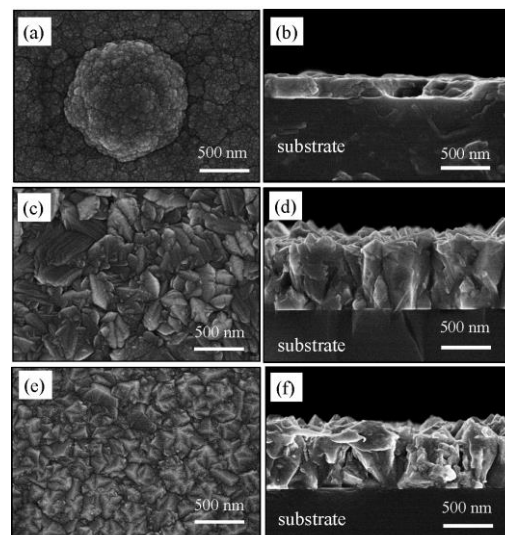


Figure 2. Planar and cross-sectional SEM micrographs of anatase TiO₂ thin films deposited with the duty cycle (a), (b) 90%; (c), (d) 70%, and (e), (f) 50% at 305°C, 266°C, and 216°C, respectively.