

X-ray Standing Wave Atomic Images of Pt Nano-Crystals Supported on SrTiO₃ (001)

S. Christensen,¹ A. Kazimirov,² M. Hersam,¹ M. Bedzyk,^{1,3}

¹ Department of Materials Science & Engineering, Northwestern University, Evanston, IL U.S.A.;² CHESS, Cornell University, Ithaca, NY U.S.A.; ³ Materials Science Division, Argonne National Laboratory, Argonne, IL U.S.A.;

Introduction

Fundamental research on the platinum/strontium titanate interface impacts many major fields including catalysis, microelectronics and thin films [1-2]. The chemical termination of the SrTiO₃ (001) may be controlled to produce either the TiO₂ or SrO stoichiometry at the surface [2,3]. For TiO₂ terminated SrTiO₃, 20 nm platinum films were shown to grow with a (001) cube on cube epitaxy [2]. DFT calculations support these experiments [4]. The minimal epitaxial strain (Pt *a*: 3.923Å; SrTiO₃ *a*: 3.905Å) reduces this study to one largely of the chemical interface. A well defined interface begins with the surface preparation. Hence, we selected the surface preparation resulting in the formation of a (2x1) surface reconstruction [5].

Methods and Materials

SrTiO₃ (001) (OKEN, Japan) was treated with NH₄F:HF buffer solution for ~30 s, then annealed at 1050°C in flowing O₂, followed by an annealing at 950°C in UHV for 30 minutes. LEED confirmed the formation of a (2x1) two domain reconstructed surface. Platinum was evaporated onto the surface in the UHV chamber while heating the substrate at 400°C. Two different Pt coverages (0.17 ML Pt and 0.60 ML) were produced for analysis.

Without removing the samples from the UHV chamber, X-ray standing wave (XSW) data was collected for the (002) SrTiO₃ Bragg reflections after a series of anneals. The samples were then removed from vacuum for XSW scans for the (001), (002), (022), and (111) Bragg reflections. Grazing incidence X-ray scattering (GISAXS) and AFM measurements followed.

Results

Annealing the substrates leads to a general increase in coherent fraction, f_{002} , of the XSW measurement. For both coverages, the coherent position, P_{002} , of Pt undergoes a large modulation between 800-900°C. Removal of samples to ambient shows a significant decrease in f_{002} for the 0.17 ML Pt coverage. Summation of the Pt Fourier components measured by the open air XSW scans allows for the creation of a direct space atomic density map [6]. For both coverages an fcc-like Pt structure results. See Fig. 1. AFM and GISAXS measurements indicate the formation of Pt nanoparticles on the surface.

Discussion

The fcc-like structure observed in the XSW atomic density maps is consistent with the findings of the 20 nm films where cube on cube (001) epitaxy on TiO₂ terminated SrTiO₃ (001) was observed [2]. This would indicate that Pt structure on TiO₂

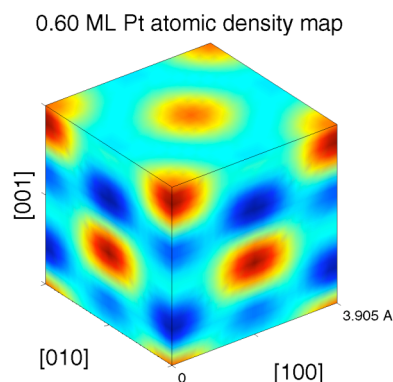


Fig. 1. Pt atomic density maps: 0.60 ML Pt.

terminated SrTiO₃ (001) forms early in the growth process at submonolayer coverage. Furthermore, AFM results from ref. [2] show the films to consist (001) oriented Pt grains. Combining this with the current results from AFM and GISAXS suggests that Pt will form small nanocrystals that grow into grains of a film as Pt is deposited.

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References

- [1] R.G. Carr and G.A. Somorjai, *Nature* **290**, 576 (1981).
- [2] A.D. Polli, T. Wagner, T. Gemming, and M. Ruhle, *Surf Sci* **526**, 107 (2003).
- [3] M. Kawasaki, K. Takahashi, T. Maeda, R. Tsuchiay, M. Shinohara, O. Ishiyama, T. Yonezawa, M. Yoshimoto, and H. Koinuma, *Science* **266**, 1540 (1994).
- [4] A. Asthagira and D.S. Sholl, *Surf Sci* **581**, 66 (2005).
- [5] N. Erdman, K.R. Poeppelmeier, M. Asta, O. Warschkow, D.E. Ellis, and L.D. Marks, *Nature* **419**, 59 (2001).
- [6] M.J. Bedzyk, *The Enclopedic Dictionary of Condensed Matter Physics* edited by G.F. Bassani, G.L. Liedl, and P. Wyder (Academic Press (Elsevier), 2005).