



Abstract ID : 65

Initial Oxidation of Ruthenium(0001) by Near Ambient Pressure X-ray Photoelectron Spectroscopy

Content

Ruthenium is known as functional material, for example as catalyst[1] or for protective coatings[2]. These applications often require ruthenium in its metallic state, whereas at elevated oxygen pressures and temperatures oxidation occurs. The oxidation of ruthenium has been extensively investigated, and interesting properties such as a high threshold pressure and autocatalytic oxidation have been observed. Prior studies show Cabrera-Mott (CM) oxidation at low temperature (20-200°C) [3], and the equilibrium oxidation states for 20-400°C in 10-2mbar O₂ with near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) [4]. The reaction for the second study proceeds too fast under those conditions to obtain information on kinetics[4]. By combining NAP-XPS at lower pressure with a broad temperature range, we limit the speed of oxidation to an observable pace and gain insights into the nature of Ru oxidation and its energetics.

In the present study, time-resolved NAP-XPS is used to follow the oxidation of a Ru(0001) single crystal during exposure to 10⁻⁴ mbar O₂ at 200-400°C. At each temperature, time-resolved NAP-XPS spectra are taken to quantify the evolution of the oxidation states of ruthenium at the surface. Using the electron attenuation length in Ru and RuO₂, an average layer thickness is calculated from the intensity ratio of the different species[5]. Time-resolved NAP-XPS in this intermediate pressure regime allows the identification of the first steps of oxidation and its pathway towards the equilibrium oxide thickness. The ruthenium spectra indicate that the rutile RuO₂ is only formed after exceeding a threshold thickness of approximately 0.6nm. We speculate that at 0.6nm, which would be two layers of a structure postulated for ultrathin Ru oxide [6], a phase change occurs towards the rutile RuO₂ phase. At higher temperatures we see a change in oxidation rate after reaching this threshold thickness, also indicating a phase change. Above this threshold thickness, oxidation proceeds at accelerated pace for high temperature.

In addition to the in-depth study of single crystal Ru(0001), a comparison to the more realistic system of polycrystalline ruthenium was made. Even after correcting for surface roughness and probing angle effects, polycrystalline ruthenium shows an increased oxide thickness in comparison to the single crystal while showing comparable kinetics. The NAP-XPS measurements indicate a transition to rutile RuO₂ at the same threshold thickness, as well as a comparable oxidation rate change.

References:

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Track Classification: Surface science/chemistry

Contribution Type: Poster contribution