Effects of surface step on Cu$_2$O thin film growth and Cu$_2$O surface reactivity

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Fundamental understanding of metal oxidation has received extensive interest due to its significant importance in many fields including high temperature corrosion, catalytic reactions and thin film processing. However, many questions still remain unresolved concerning the early stages of oxidation, which is inaccessible by the traditional surface science and “bulk” materials science techniques. The nucleation and growth of surface oxide is often complicated by surface inhomogeneities caused by the presence of surface defects such as steps. In this work, through the use of in-situ transmission electron microscopy (TEM) we observe that the presence of surface steps leads to the decomposition of the Cu$_2$O overlayer at the growth front of the Cu substrate, thereby resulting in oscillatory Cu$_2$O film growth. Using density-functional theory (DFT) total energy calculations and ab initio molecular dynamics (AIMD) simulations, we show that oxygen adsorption on the lower terrace destabilizes the Cu$_2$O thin film formed on the upper terrace that leads to oxide decomposition. Our results reveal the unique role of surface defects in oxide film growth and may have broader implications for understanding the fundamental process governing gas-surface reaction kinetics as modulated by atomic defects on a solid surface [1]. We will also discuss the effects of step edge on the surface reactivity of Cu$_2$O, revealed via DFT calculations of gas species adsorption on the terrace and step edges of Cu$_2$O surfaces.