# Plasma Oxidation of Copper: Molecular Dynamics Study with Neural Network Potentials

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## Introduction

Copper became the universal material of choice for interconnects in integrated circuits. Due to challenges involved in dimension scaling, the semiconductor industry is looking for an atomic-level engineering approach that is simultaneously capable of achieving high selectivity and high directionality. One of the most promising techniques for this purpose is atomic layer etching (ALE). On the copper metal, the process requires controlled conversion of the surface layers of copper to copper oxide under oxygen plasma. However, the current implementation leads to relatively thick activated layers without being self-limiting, preventing a finer grain of control over etch per cycle (EPC) from being achieved.[1]

The interaction of metal surfaces with the plasma is unique in having energetic particles impacting the surface.[2] Combination with the diverse environments encountered during the oxidation process makes it difficult for classical force fields to describe accurately with their limited functional forms. In the present work, we exploit the flexibility of high-dimensional neural network potential (HDNNP) to describe the binary interaction of copper and oxygen on the density functional theory (DFT) potential energy surface. The potential is used to perform molecular dynamics, the analysis of which yields suggestions on improving the existing experimental process.

## Materials and Methods

DFT calculations are performed with the Vienna Ab-initio Simulation Package (VASP) within the projector-augmented wave (PAW) method.[3] The PBE exchange correlation functional was used.[4] The neural network potential training and prediction is performed using the n2p2 package. The molecular dynamics simulation was performed using LAMMPS.

## Results and Discussion

In Figure 1a, the thickness of the oxide, as characterized by the automated analysis method, is shown. The growth curves separate into two strands at the beginning of growth, with the growth rate determined by the availability of oxygen (triangle vs. cross markers). In the simulation, this corresponds to the neutral-to-ion ratio, since the ions are deposited at a fixed rate across these simulations). This is a sign indicating a high sticking probability when surface is predominantly metallic copper. As oxide becomes thicker, less copper atoms are exposed, and the growth gradually transforms to be kinetic energy limited, as indicated by the different two strands (red vs. black lines).

In Figure 1b, a more direct comparison is obtained if the ions/neutrals are stopped midway in the simulation. It can be seen that stopping either slows down the simulation signficantly, but the effect of stopping ion is much more immediate and more pronounced. These and other evidence suggest oxide growth is thermally activated, with the local heating from ion impacts as a significant energy source.

In Figure 1c, an snapshot of one of the MD trajectories is shown (side view). The oxide here is around 2nm thick, with lateral dimensions of 5nm-by-5nm.

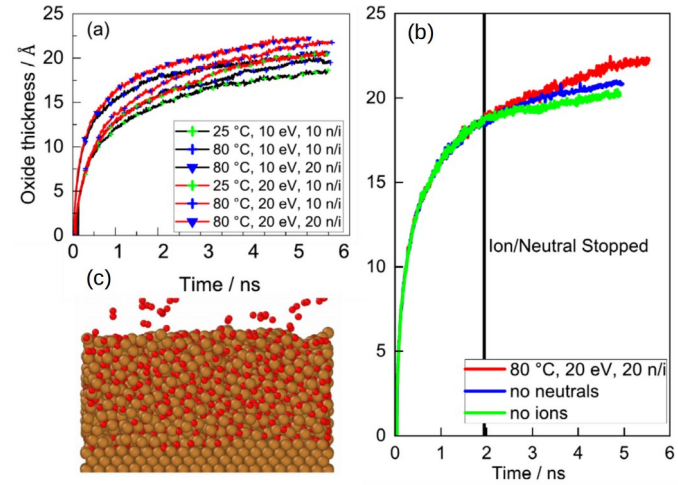


**Figure 1.** (a): oxide thickness vs. time. The parameters in the legend indicate temperature, kinetic energy of ion, and the ratio of neutral to ions. (b): the effect of using only neutral or only ions, as compared to using both. (c): a side view of the MD simulation slab.

## Significance

This work provides a valuable computational tool for studying copper oxidation (plasma and thermal), as well as a potential general framework for developing binary plasma-surface interaction models.

## References

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