

## Nucleation and growth mechanism of graphene on copper

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Chemical vapor deposition (CVD) of graphene on copper has enabled growth over large areas and its implementation into electronics. Copper has been demonstrated to be better for the industrial scale production of graphene than the most of transition metal catalysts as the growth is limited to a monolayer due to low solubility of carbon in copper and the possibility to easily transfer graphene onto insulating substrates via etching of copper [1,2]. Graphene growth on copper occurs via nucleation sites in which the nuclei grow radially and eventually coalesce into a continuous sheet of polycrystalline graphene. The CVD graphene is defective, consisting of grain boundaries that are responsible for the diminished electronic properties compared to mechanically exfoliated graphene [3,4]. Despite the tremendous interest in graphene, the basic physicochemical parameters that control the nucleation and growth during deposition are poorly understood, hindering the realization of wafer-scale single crystal graphene films.

Here, we develop the model of nucleation and growth kinetics of CVD graphene on copper by systematically analysing the evolution of graphene growth for different growth conditions - temperature, pressure, substrate crystal orientations, and surface roughness. We have identified that graphene nucleus density decreases with increase in the growth temperature through two different regimes of thermally activated processes. In addition, graphene growth stops without forming a continuous layer at the later stage of growth for low growth temperatures.

Our model shows that graphene arises from the crystallization of a supersaturated fraction of carbon-adatom species and the nucleation density is the results of interplay among various atomic processes such as carbon adsorption and desorption, surface diffusion, and carbon adatom capture at the edges of growing nuclei. As these processes are thermally activated with different activation energies, there is a transition in nucleation mechanism from capture controlled nucleation at low temperatures (<870 °C) to desorption controlled nucleation at high temperature (> 870 °C). In all cases, Cu surface features such as Cu step edges, grain grooves, and undulations significantly influence the nuclei and nucleus density by providing preferential nucleation sites.

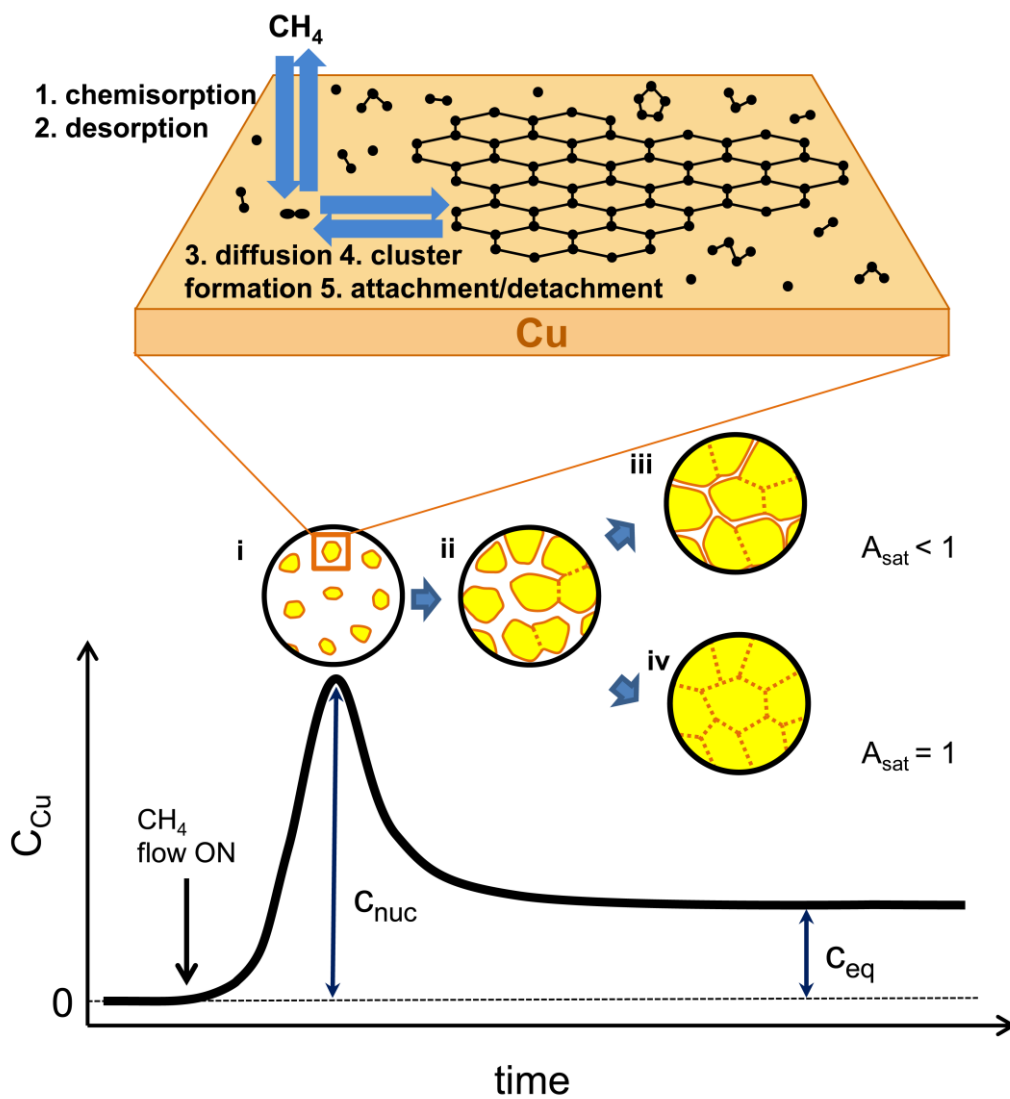
On the other hand, the rate-limiting step for the growth of graphene was found to be the attachment of carbon adatom species to the graphene edges and did not depend on the crystal orientation of the substrate. The saturation of graphene area below a complete coverage can be explained by the balance of attachment and detachment rates at the graphene edges as the level of surface carbon reaches an equilibrium level.

The knowledge of the supersaturation concentration of carbon adatoms at the onset of nucleation gives guidance for selection of growth conditions that enables predictions whether a continuous, pinhole-free graphene film would be produced. These results provide new fundamental insights that will allow the design of the scalable synthesis of high-quality graphene.

## References

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## Figures



Overall illustration of the nucleation and growth mechanism of graphene on Cu.