# Sublayer Carbonation of Ni(111) Surfaces from the Boudouard Reaction: An STM Study

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Carbon formation on Ni surfaces is essential to many cutting-edge studies and applications in nanomaterials fabrications and heterogeneous catalysis, including 2D and 3D graphene growth,[1] methanation of $CO_2$ and biomass gas, and reforming of methane. Understanding the initial carbonation of a nickel surface at an atomic level will provide insights into controlling the chemical processes relating to carbon-nickel interactions. Herein, the initial formation of surface carbon adsorbates and carbides on Ni(111) from the Boudouard reaction ($2CO \leftrightarrow CO_2 + C$) is studied by scanning tunneling microscopy (STM) under ultrahigh vacuum (UHV) conditions at room temperature.

The initial carbon formation occurs at both step-edge and terrace sites, leading to completely different island structures. The quasi-square pattern formation on the step edge (Fig. 1A) follows along the $[01\bar{1}]$ direction and is thus different from the $(\sqrt{39} \times \sqrt{39})R16.1°$ model.[2] The carbon atoms absorbed on terraces either form 1D lines that are templated by Ni(111) substrate (Fig. 1B) or form small clusters (Fig. 1C) that agree with the theoretical prediction of carbon clusters on Ni(111).[3] The terrace features are mobile at room temperature, while the step edge features are fixed.

As the coverage of surface carbon increases, the quasi-square pattern expands from step edges, and simultaneously, a second layer of nickel carbide forms, featuring a linear Moiré pattern (Fig. 2).[4] The first layer of carbon adsorption presents a unit cell that is 30° rotated from that of Ni(111) and mediates the migration of substrate Ni atoms to a carbide phase.

In summary, the STM study, potentially supported by density functional theoretical calculations, demonstrates the initial growth of surface carbon on Ni(111) by the Boudouard reaction. When forming islands from step-edge sites, the absorbed carbon induces the Ni surface to reconstruct and create four-fold coordinates that are essential for carbide formation. Without the reconstruction of the Ni substrate, the adsorbed carbon chains and clusters are weakly bound to terraces and mobile.

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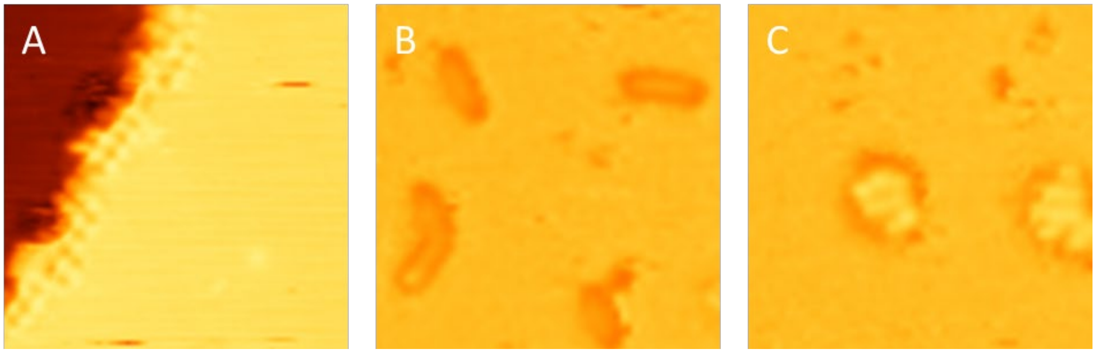

Figure 1: Initial carbon formation on Ni(111) imaged by STM: A) quasi-square pattern formed along a step edge; It = 0.3 nA; V = 0.8V B) 1D lines along Ni(111) close-packed directions; It = 0.3 nA; V = 1.3V C) carbon cluster on Ni(111) terrace; It = 0.3 nA; V = 1.3V. All image sizes are 10 × 10 nm$^2$.

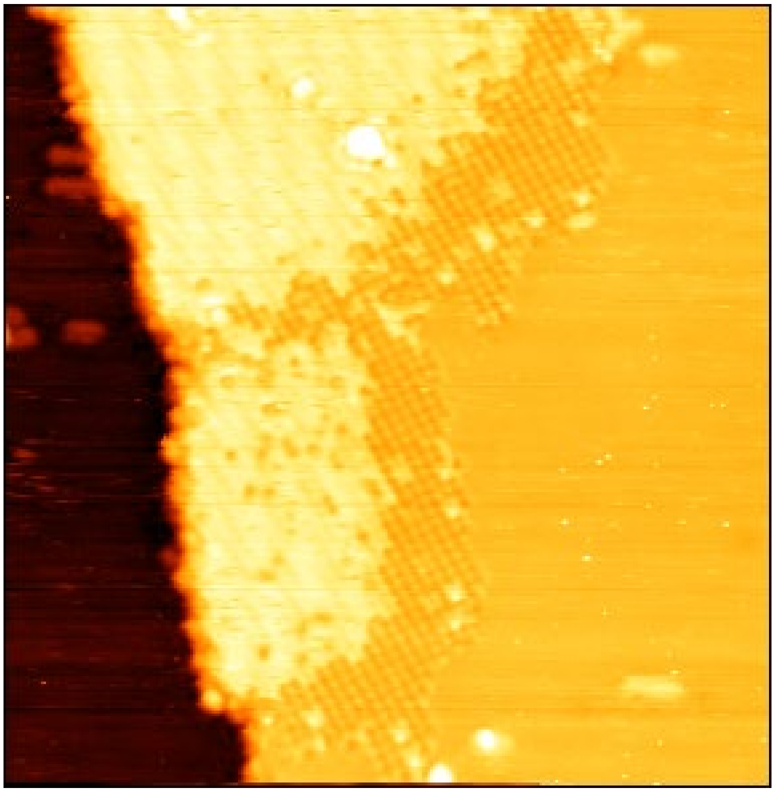

Figure 2: An STM image of nickel carbide next to an island of carbon adsorption. Image size: 30 × 30 nm$^2$. It = 0.3 nA; V = 1.3V.