

Influence of the defect density on the ordering of an NHC monolayer on a silicon surface

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Silicon is the element of choice in semiconductor devices and a functionalization of silicon surfaces is highly desirable for electronic industries. N-Heterocyclic carbenes (NHC) have been demonstrated to be promising modifiers and anchors for surface functionalization, but so far mainly on metal surfaces. Only recently, the formation of ordered NHC monolayers on silicon was demonstrated [1,2].

Here, the adsorption behavior of cyclohexyl cyclic (alkyl)(amino)carbene (cyCAAC) molecules (see Fig. 1(a)) on the Si(111)($\sqrt{3}\times\sqrt{3}$)R30°-B surface is investigated using scanning tunneling microscopy (STM), low energy electron diffraction, and X-ray photoelectron spectroscopy.

Surprisingly and quite unexpected on semiconductors, we find a self-limited, well ordered growth of a stable monolayer with large domains (see Fig. 1(b)). The overlayer is characterized by a 3×3 periodicity and an upright adsorption geometry of the molecules [2].

The defect density of the substrate thereby strongly influences the grade of ordering in the monolayer. While large ordered domains form on substrates with low defect densities, only much smaller domains are observed on high defect density substrates (see Fig. 1(c)). This shows that the initial adsorption of the molecules takes place on a defect site. In the studied material system the defect density of the substrate thus directly determines the domain sizes [2].

Moreover, the cyCAAC monolayer leads to a strong work function reduction and exhibits a good thermal stability demonstrating its functionalization capability.

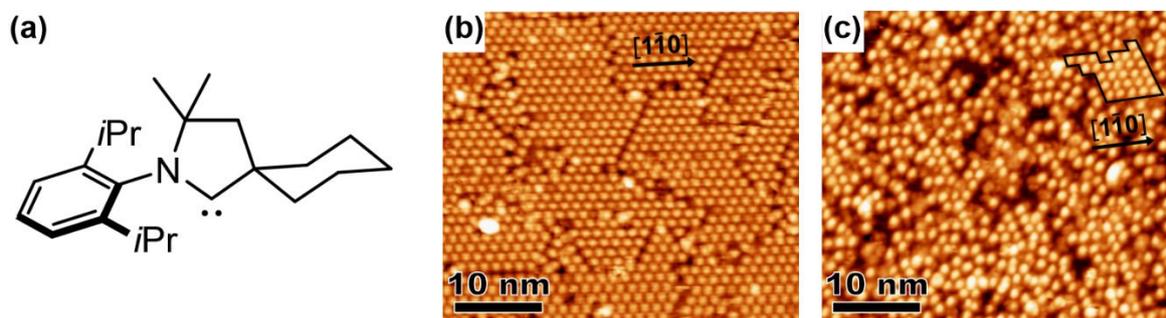


Fig. 1. (a) Structure of the cyCAAC molecule investigated in this work. (b) Overview STM image of the highly ordered cyCAAC monolayer on the low defect density substrate showing a 3×3 periodicity. (c) Overview STM image of the cyCAAC monolayer on a high defect density substrate showing much smaller domains.

[1] M. Franz et al., Nat. Chem. **13**, 828 (2021).

[2] R. Zielinski, M. Das, C. Kosbab, M. T. Nehring, M. Dähne, N. Esser, M. Franz and F. Glorius, J. Mater. Chem. C, 2023, DOI: 10.1039/D3TC00681F.