

# Self-assembled growth of C<sub>60</sub> monomolecular layers at Tl/NiSi<sub>2</sub> atomic sandwich on Si(111)

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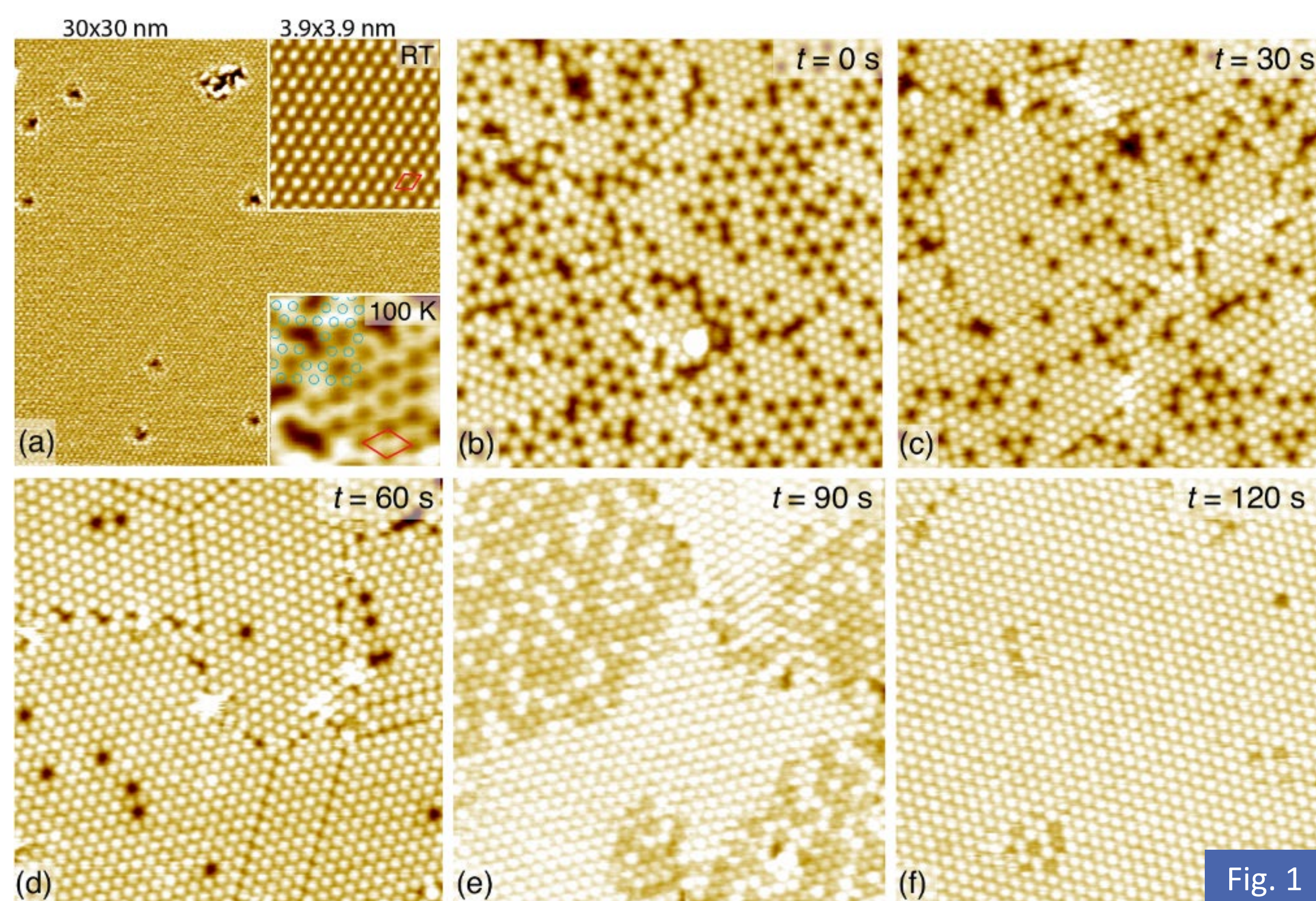
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## Introduction

The molecular self-assembly has been extensively investigated owing to its great potential for a wide range of applications. Due to its spherical shape and high symmetry, C<sub>60</sub> has been considered an ideal molecule for studying self-assembly process on crystalline surfaces. As examples, one can remind fabrication of the molecular arrays almost exclusively built of the magic clusters on the In-modified Au/Si(111) surface [1], self-assembled C<sub>60</sub> ordering into the unusual "trilliumene" structures on Si(111) and Ge(111) surfaces covered by monolayers of Tl or Pb [2,3]. The discovery of graphene has caused a strong increase of the interest in 2D materials having a thickness of one atomic layer. These materials are considered as promising candidates for the synthesis of supramolecular systems, including those containing C<sub>60</sub> fullerenes [4,5]. This served as an additional motivation for considering in this study the self-assembly of C<sub>60</sub> on the Tl/NiSi<sub>2</sub>/Si(111) sandwich. The upper atomic layer is represented in this sandwich by a Tl monolayer. In the Tl/NiSi<sub>2</sub>/Si(111) system, the Tl coating can decrease to ~0.6 ML without the formation of new reconstructions. Using the possibility of changing the Tl coating, the effect of the Tl atomic density on the structure of the C<sub>60</sub> layers was investigated.

## Experimental results

Fig. 1 shows a set of STM images illustrating the evolution of the surface structure after each step of Tl deposition for 30 s. at a rate of 0.14 ML/min onto the C<sub>60</sub> monolayer grown on the Tl/NiSi<sub>2</sub>/Si(111) surface with 0.73 ML of Tl. The original Tl/NiSi<sub>2</sub>/Si(111) surface shown in Fig. 1(a). As can be seen, arrays of fullerenes contain "holes" arranged in the  $\sqrt{3}\times\sqrt{3}$  lattice inside a fullerene layer. This coincides with the periodicity of  $\sqrt{21}\times\sqrt{21}$  in the lattice constants Si(111),  $a_{\text{Si}} = 0.384$  nm, since the C<sub>60</sub> layer has a periodicity of  $\sqrt{7}\times\sqrt{7}$ .



In the current case the "holes" are fullerenes located lower than their neighbors. We called such molecules "dark", and the molecules around them with normal brightness — "normal". Deposition of Tl at RT on this surface led to a gradual decrease in the density of dark fullerenes and after total deposition for 60 s. the dark molecules completely disappeared, and the arrays began to consist only of normal fullerenes. With further deposition of Tl, "bright" fullerenes begin to appear, their number increases in proportion to the dose of Tl, eventually all regions consist only of such bright molecules (Fig. 1(f)).

The STM profiles along the lines crossing the fullerenes of different types, dim and normal, (Fig. 2(a,b)) show that apparent height for the normal fullerenes is by ~0.29 nm greater than that for the dim fullerenes. Analysis taken on the C<sub>60</sub> island helps to prove that the depressions are the dim fullerenes but not vacancies, since one can notice occurrence of the similar dim fullerenes at the periphery of the C<sub>60</sub> island. The height difference remains after changing the STM bias polarity (Fig. 2(a,b)), indicating that this difference is associated mainly with the topography. Similar analysis conducted for the normal and bright fullerenes reveals that the bright fullerenes are by ~0.06 nm higher than the normal fullerenes (Fig. 2(c,d)). Thus, one can conclude that there are three distinct height levels which fullerenes can occupy on the Tl/NiSi<sub>2</sub>/Si(111) substrate and upon increasing atomic density of the Tl monolayer the fullerenes progressively change their location for the levels of the greater height. Conducting calibration experiments to convert the deposition time of Tl into coating gave an understanding of the origin of dark, normal and bright fullerenes. The difference in the brightness of C<sub>60</sub> molecules is related to the number of Tl atoms under an individual fullerene.

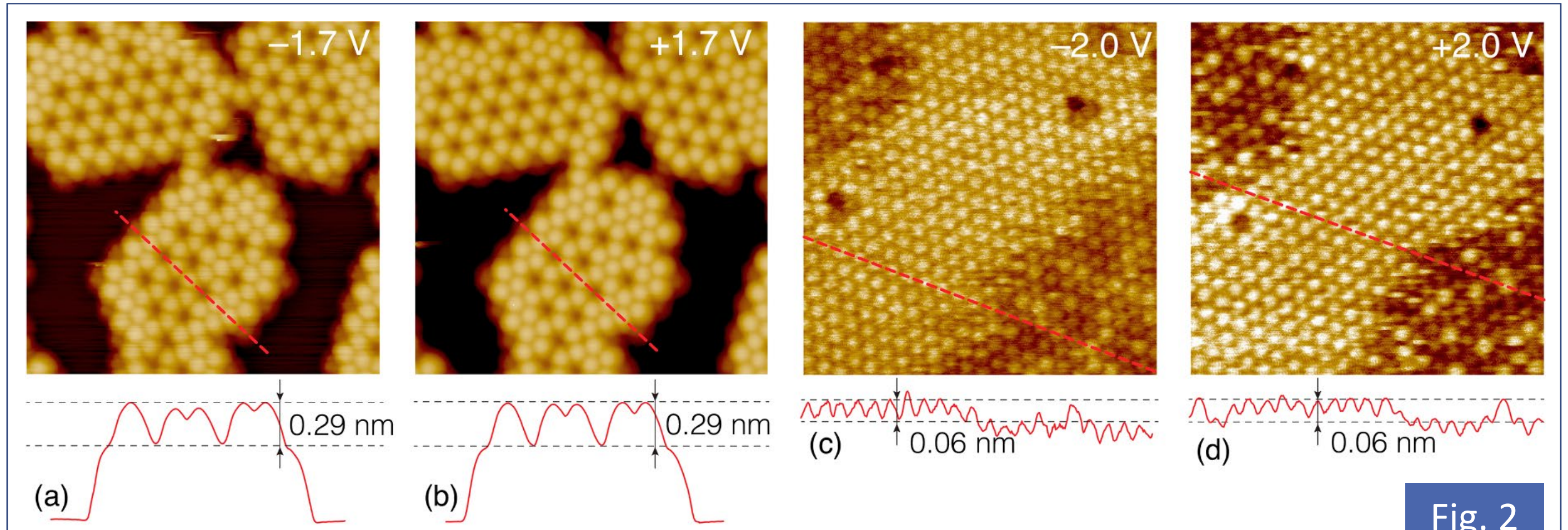


Fig. 2

Using DFT calculations, structural models of C<sub>60</sub> on Tl/NiSi<sub>2</sub>/Si(111), which adsorption sites and orientation of C<sub>60</sub> fullerenes were varied, as well as the number of Tl atoms under them, were tested. It was found that C<sub>60</sub> occupy T<sub>4</sub> positions, which are preferable over the T<sub>1</sub> and H<sub>3</sub> positions, and are oriented with a hexagon upwards. As for the number of Tl atoms, the single model that corresponds to the experimental data is shown in Fig. 3.

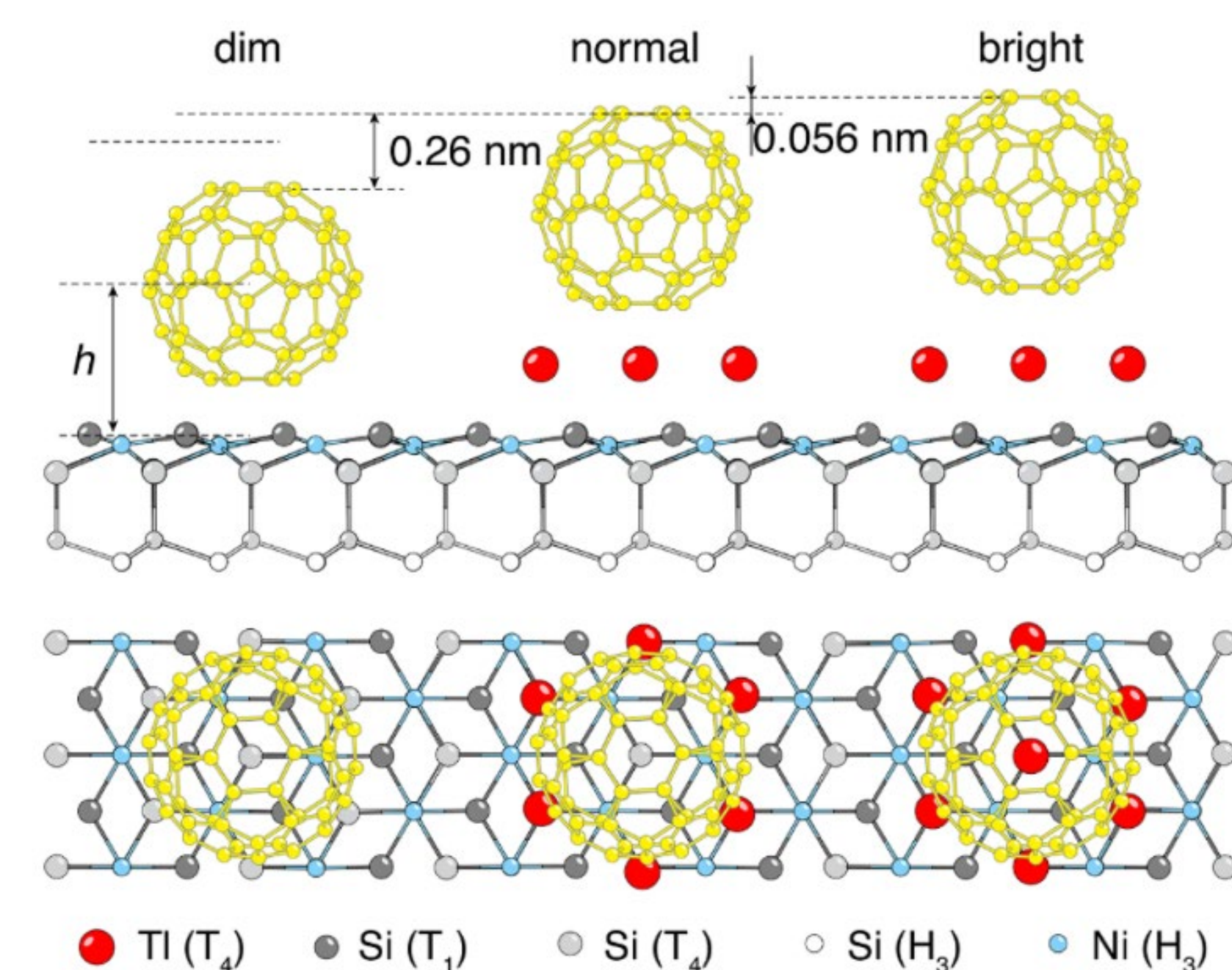


Fig. 3

It was concluded that there are completely lack Tl atoms under dark fullerene, one thallium atom is missing under normal fullerene, and all 7 atoms sit in their places under bright fullerene. Accordingly, it was calculated that normal fullerenes are 0.26 nm above the dark and 0.056 nm below the bright. Using information about the number of Tl atoms under each of the fullerenes, STM images were processed to assess the Tl coating at each stage of Tl deposition. The obtained results coincided with the calibration data, thereby confirming the reliability of the calculated models.

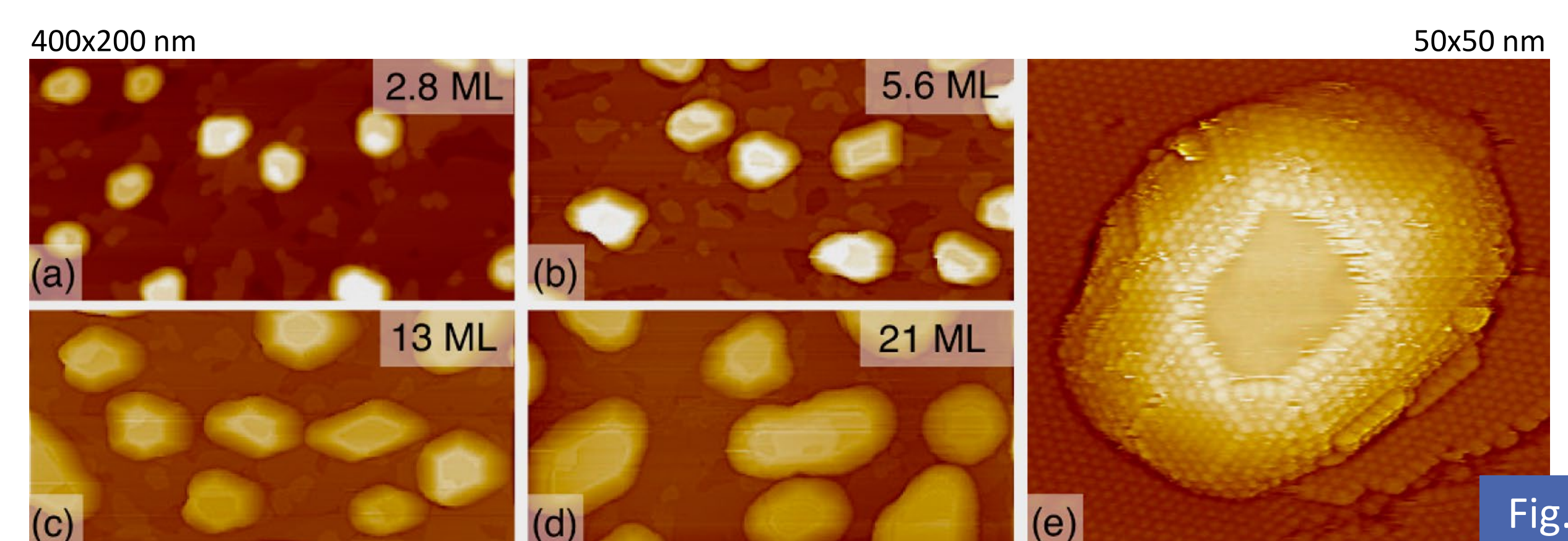


Fig. 4

When the Tl monolayer beneath the C<sub>60</sub> layer is completed, all fullerenes become bright. If Tl deposition is continued further, the Tl layer does not adopt extra atoms and they agglomerate into the 3D islands beneath a fullerene layer (Fig. 4). The Tl islands have a flat top and epitaxial crystalline structure, and the separation of islands is ~100 nm.

## Conclusions

Using STM observations and DFT calculations we have examined self-assembled formation of C<sub>60</sub> monomolecular layers on the surface of the atomic Tl/NiSi<sub>2</sub>/Si(111) sandwich. Deposited C<sub>60</sub> fullerenes form hexagonal close-packed arrays. Within the C<sub>60</sub> layer, the fullerenes display three distinct types of contrast in the STM images, depending on the amount of thallium under them. The fraction of fullerenes of each type can be changed in controllable way using Tl deposition onto the C<sub>60</sub>/Tl/NiSi<sub>2</sub>/Si(111) sample. Bearing in mind that single-layer NiSi<sub>2</sub> possesses advanced metallic properties [6], elucidating the effects produced by Tl overlayers of various atomic densities and C<sub>60</sub> layers with various separations from a single-layer NiSi<sub>2</sub> are of interest for examine the peculiarities of the electronic transport in the layered atomic structures. Possibility for growing thick C<sub>60</sub> films as protective layers for the buried atomic sandwich allows to conduct *ex situ* transport measurements, the topic of interest for both fundamental research and the advancement of electronic applications.

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## References:

- [1] Gruznev D. et al. Nat. Commun. 4, 1679 (2013).
- [2] Zotov A. et al. J. Chem. Phys. 149, 034702 (2018).
- [3] Mihalyuk A. et al. J. Chem. Phys. 154, 104703 (2021).
- [4] Kumar A. et al. Nanotechnology 28, 082001 (2017).
- [5] Mirzayev R. et al. Sci. Adv. 3, E1700176 (2017).
- [6] Bondarenko V. et al. 2D Mater. 7, 025009 (2020).