## **PAPER • OPEN ACCESS**

## Adsorption structure of Bi on the fivefold surface of i-Ag-In-Yb quasicrystal

To cite this article: Kazuki Nozawa and Yasushi Ishii 2017 J. Phys.: Conf. Ser. 809 012018

View the article online for updates and enhancements.

## You may also like

- The atomic structure of the threefold surface of the icosahedral Ag-In-Yb <u>quasicrystal</u> C Cui, P J Nugent, M Shimoda et al.

- The atomic structure of ternary amorphous <u>Ti, Si<sub>1</sub>,O<sub>2</sub> hybrid oxides</u> M Landmann, T Köhler, E Rauls et al.
- AMGCN-L: an adaptive multi-time-window graph convolutional network with longshort-term memory for depression detection

Han-Guang Wang, Qing-Hao Meng, Li-Cheng Jin et al.





**DISCOVER** how sustainability intersects with electrochemistry & solid state science research



This content was downloaded from IP address 3.17.184.90 on 08/05/2024 at 02:57

IOP Conf. Series: Journal of Physics: Conf. Series 809 (2017) 012018

# Adsorption structure of Bi on the fivefold surface of i-Ag-In-Yb quasicrystal

## Kazuki Nozawa<sup>1</sup> and Yasushi Ishii<sup>2</sup>

 $^1$  Department of Physics and Astronomy, Kagoshima University, Korimoto, Kagoshima 890-0065, Japan

<sup>2</sup> Department of Physics, Chuo University, Kasuga, Tokyo 112-8551, Japan

E-mail: kazuki.nozawa@gmail.com

**Abstract.** The initial stage of the growth of a Bi overlayer on the fivefold surface of icosahedral Ag-In-Yb quasicrystal is studied using the first-principles density functional calculation. Comparing to the previous study about Pb adsorption on the same surface, it turns out that Bi is bound stronger than Pb on the surface, and small differences are found in the relative magnitude of the adsorption energy of some stable sites. Those may lead some differences in the sequence of the growth in the initial stage, it is concluded that the under- and first-layers observed in the growth of Pb are formed also in the Bi case.

#### 1. Introduction

After the discovery of stable quasicrystals (QCs) [1], studies on the QC surfaces were started by several groups. Studies of clean surfaces revealed an important feature that, after proper sputter-annealing treatment, the surfaces recover the quasi-periodic atomic arrangement same as the bulk [2, 3, 4]. It stimulated studies that aim at fabricating single element QC using the existing QC surfaces as a template. Following the success by Franke *et al.* [5], quasiperiodic monolayers have been obtained in several systems so far [6, 7, 8, 9, 10].

In addition to these development, we recently succeeded in fabricating quasi-periodic multilayered Pb film on the fivefold surface of the icosahedral (i-)Ag-In-Yb quasicrystal, and revealed that the Pb overlayers grow with imitating the atomic structure of the substrate QC [11].

In this paper, we study the initial stage of the single element QC growth using Bi as the adsorbate instead of Pb used in the previous study.

#### 2. Methods and Calculations

In this paper, we calculate the adsorption energy of Bi adsorbed on the clean surface of the fivefold surface of i-Ag-In-Yb based on the density functional theory (DFT). The quasicrystalline substrate is isostructural to the binary i-Cd-Yb QC, where Cd is replaced by Ag and In. In order to handle the aperiodic surface within the DFT, the fivefold surface of the i-Ag-In-Yb was approximated by a disk-shaped cluster extracted from a QC model by Takakura *et al* [12]. The adsorption energy is defined as

$$E_{\rm ads}(\boldsymbol{r}) = E_{\rm substrate+atom}(\boldsymbol{r}) - \left[E_{\rm substrate}(\boldsymbol{r}) + E_{\rm atom}(\boldsymbol{r})\right],\tag{1}$$

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

Published under licence by IOP Publishing Ltd

where r = (x, y, z) is the position of Bi considered (x and y are the lateral positions, and z is the distance with the surface), and  $E_{\text{substrate}+\text{atom}}$  is the total energy of the system that Bi adsorbed on the substrate.  $E_{\text{substrate}}$  and  $E_{\text{atom}}$  are the total energies of the isolated substrate and Bi atom, respectively. The adsorption energy is calculated on a 0.5 Å  $\times$  0.5 Å grid, and interpolated using the cubic spline method. No structural relaxation has been carried out for both adsorbate and surface atoms. The atomic position of the adsorbate is changed manually on the grid points one-by-one. It should be noted that the disk-shaped cluster is not common for all calculations, but it is re-defined as the cluster center is always located just below the adsorbate. The size of the disk-shaped cluster is 4Å thickness and 30Å diameter. A simulation box of 40 Å  $\times$  40 Å  $\times$  18 Å is used for the supercell calculation. The calculation is carried out using the VASP program package [13]. The projecter-augumented-wave potentials [14, 15] are used to describe the interaction between the electron and ionic core. The 4f-electrons of Yb atom is kept frozen in the core. The generalized gradient approximation is adopted for the exchange-correlation term [16]. Non-spin polarized calculations are used. In order to estimate the errors in the calculation, we compared the adsorption energies at several sites calculated using the following systems.

- (i) 6 Å thickness and 30 Å diameter cluster + 40 Å  $\times$  40 Å  $\times$  18 Å simulation box
- (ii) 4 Å thickness and 40 Å diameter cluster + 50 Å  $\times$  50 Å  $\times$  18 Å simulation box
- (iii) 4 Å thickness and 30 Å diameter cluster + 50 Å  $\times$  50 Å  $\times$  18 Å simulation box
- (iv) 4 Å thickness and 30 Å diameter cluster + 40 Å  $\times$  40 Å  $\times$  26 Å simulation box

According to these tests, it turns out that the adsorption energy is almost converged for the lateral size of the disc-shaped cluster and the size of the simulation box. Relatively large differences in the adsorption energy are found when we change the cluster thickness (i). The difference is less than 0.1 eV for most sites, and about 0.2 eV at worst. The differences originated in the lateral size of the cluster and the size of the simulation box are one oder of magnitude smaller than these. The cubic spline interpolation cause a large error at some sites where the adsorbate-surface interaction is strongly repulsive, but such site is not crucial to find out the stable adsorption sites, and, therefore, it does not affect our conclusion.

Since QC does not have the translational periodicity, there are infinite number of candidates for the surface top layer. Thus, we use a dense and Yb-rich surface as the surface top layer according to the experimental findings [17]. The fractionally occupied sites are treated in the same way with our previous paper [11]. Figure 1(a) is the atomic structure of the surface top layer used in the calculation. The red and green spheres denote the In and Yb atoms, respectively. A structure that In-decagon surrounded by ten Yb-pentagons highlighted in blue is commonly found in this plane. We focus on the area around this structure in this paper.

## 3. Results and Discussions

Figures 2 (a), (b) and (c) show the adsorption energies of Bi at z = 1.5Å, 1.0Å and 0.5Å, respectively. Since there is a local fivefold rotational symmetry around the centre of the area considered, we reduced the number of the sites to be calculated using the symmetry. Namely, we calculated the adsorption energies only for the sites in the first quadrant (x, y > 0). The energies of the rest sites are represented by those of the symmetry equivalent sites in the first quadrant.

One can find ten adsorption pathways (dark blue region) forming a decagon around the centre of figure 2(a) (just inside the Yb-decagon). These adsorption pathways are classified into two groups labeled A and B by the symmetry and local environment. The numbers following the labels in the figures stand for the distance between the Bi atom and the surface top layer (ten



**Figure 1.** (a) The atomic structure of the topmost surface layer used in the calculation. (b) The adsorption structure of Pb overlaid on (a).

times z). The adsorption pathway labeled A extends vertically to the surface, and ends at around A10. On the other hand, the pathway B turns outward and takes the minimum value at around B05. Figure 3(a), which is the cross section of figure 2 along y = 0 line, shows it more clearly.

Similar structure of the adsorption energies can also be found in those of Pb adsorbing onto the same surface [11]. Figure 3(b) show the adsorption energies of Pb/i-Ag-In-Yb corresponding to figure 3(a) of Bi. In addition to the general tendency that Bi is bound to the surface stronger than Pb, the energy difference between A15 and B15 may make a difference in the sequence of the growth of the overlayer. The energy difference of the A15 and B15 sites of Pb is about 0.36 eV, and we concluded in previous report that the pentagonal *first-layer* composed of Pb atoms adsorbed on A10 sites are formed before formation of the *under-layer* comprised of Pb atoms adsorbed on B05 and other sites [11]. For Bi adsorbates, the energy difference between A15 and B15 is small (about 0.07 eV) to argue the stability of the adsorption pathway. Therefore, the sequence of the formation of the first- and under-layers of Bi can not be determined by these results.

However, the sequence of the formation of these layers may not be important for the final structure of the Bi overlayer, because, according to our previous calculations [18], the preadsorbed Pb on the A10 sites dose not prevent the next Pb atom from adsorbing onto the B05 sites. Thus, eventually, the first- and under-layers are expected to be formed like the Pb case shown in figure 1(b). Here the orange and purple spheres denote the adsorbate atoms occupied the A10 and B05 sites, respectively. Roughly estimated densities of A10 and B05 sites on the surface are about  $0.6 \times 10^{-3} \text{ Å}^2$  and  $2.2 \times 10^{-3} \text{ Å}^2$ , respectively. The density of the A10 sites agrees very well to the experimental value for the Pb adsorbate ( $0.4 - 0.7 \times 10^{-3} \text{ Å}^2$ ) [11].

Consequently, we conclude that there are no significant differences between the adsorption energies of Pb and Bi on the clean surface. Thus it is expected that Bi grow like Pb at least in its initial stage. An experiment carried out recently using scanning tunneling microscopy (STM) has observed different structures with the Pb case [19]. A possibility can be pointed out that the under- and first-layer of Bi have not been detected by STM like the under layer in the Pb case, and the observed layers may be formed on these undetected layers. Further theoretical investigations are required to check the hypothesis.



**Figure 2.** Calculated adsorption energies at (a) z = 1.5Å, (b) z = 1.0Å and z = 0.5Å. Characters A and B denote the prospective adsorption pathways (see text).



Figure 3. (a) Cross sections of figure 2 along the y = 0 line. (b) Same as (a) for Pb.

## 4. Concluding remarks

The stable adsorption structure on the clean surface of the fivefold surface of the i-Ag-In-Yb QC was studied using the first-principles density functional calculation. Calculated energy surfaces show that Bi atoms are bound stronger than Pb atoms, and imply slightly different adsorption behavior with Pb. However, those also indicate that the expected adsorption structure at the initial stage is very similar to the Pb case, where the pentagonal first-layer and the under-layer filling the interstitial region of the first-layer are formed.

## Acknowledgments

The authors appreciate fruitful discussions with H. R. Sharma, M. Shimoda and A.P. Tsai. We are also grateful to H. Takakura for providing us with the atomic positions of i-Cd-Yb. Calculations are partly carried out using the supercomputer facilities at the National Institute for Materials Science, Tsukuba, and Yukawa Institute, Kyoto University.

## References

[1] Tsai A P 2003 Acc. Chem. Res. 36 31

- [2] Ledieu J, McGrath R, Diehl R D, Lograsso T A, Delaney D W, Papadopolos Z and Kasner G 2001 Surf. Sci 492 L729-L734
- [3] Sharma H R, Fournée V, Shimoda M, Ross A R, Lograsso T A, Tsai A P and Yamamoto A 2004 Phys. Rev. Lett. 93 165502
- [4] Sharma H R, Shimoda M, Sagisaka K., Takakura H, Smerdon J A, Nugent P J, McGrath R, Fujita D, Ohhashi S and Tsai A P 2009 Phys. Rev. B 80 121401
- [5] Franke K J, Sharma H R, Theis W, Gille P, Ebert Ph and Rieder K H 2002 Phys. Rev. Lett. 89 156104
- [6] Ledieu J, Leung L, Wearing L H, McGrath R, Lograsso T A, Wu D and Fournée V 2008 Phys. Rev. B 77 073409
- [7] Deniozou Th, Ledieu J, Fournée V, Wu D M, Lograsso T A, Li H I and Diehl R D 2009 *Phys. Rev. B* **79** 245405
- [8] Smerdon J A, Leung L, Parle J K, Jenks C J, McGrath R, Founée V and Ledieu J 2008 Surf. Sci. 602 2496-2501
- [9] Sharma H R, Shimoda M, Ross A R, Lograsso T A and Tsai A P 2005 Phys. Rev. B 72 045428
- [10] Shukla A K, Dhaka R S, D'Souza S W, Singh S, Wu D, Lograsso T A, Krajči M, Hafner J, Horn K and Barman S R 2009 Phys. Rev. B 79 134206
- [11] Sharma H R, Nozawa K, Smerdon J A, Nugent P J, McLeod I, Dhanak V R, Shimoda M, Ishii Y, Tsai A P and McGrath R 2013 Nature Commun. 4 2715
- [12] Takakura H, Gomez C P , Yamamoto A, de Boissieu M and Tsai A P 2007 Nat. Mater. 6 58
- [13] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
- [14] Blöchl P E 1994 Phys. Rev. B 50 17953
- [15] Kresse G K and Joubert J 1999 Phys. Rev. B 59 1758
- [16] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
- [17] Sharma H R, Shimoda M, Sagisaka K, Takakura H, Smerdon J A, Nugent P J, McGrath R, Fujita D, Ohhashi S and Tsai A P 2009 Phys. Rev. B 80 121401(R)
- [18] Nozawa K and Ishii Y 2011 Philos. Mag. 91 2913
- [19] Sharma H R et al. to be published.