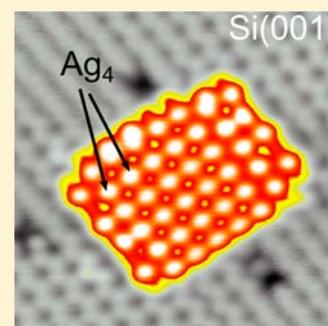


Identification of Tetramers in Silver Films Grown on the Si(001) Surface at Room Temperature

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Supporting Information

ABSTRACT: We describe the atomic structure of the silver film grown on Si(001) at room temperature, as studied by low-temperature scanning tunneling microscopy and density functional theory. Experiment and theory agree on a film structure in which Ag tetramers are identified for the first time. Ag tetramers are found to be adsorbed exclusively at the trough between two Si rows, interacting with four adjacent Si dimers via covalent bonding. Consequently, the π bonds of the Si dimers underneath the silver film are eliminated.



The growth of metal films on silicon is of interest in the fabrication of miniaturized semiconductor devices, including integrated circuits, microelectronics, and optoelectronics.^{1–4} Among the numerous systems in this field, the growth of Ag films on silicon has been heavily examined,^{5–21} because it serves as a prototype model for an abrupt metal/semiconductor interface. Much of this work has been focused on the Ag/Si(111) system, with the $\sqrt{3} \times \sqrt{3}$ surface reconstruction having been studied in particular detail.^{22–26} Much less work has been done for Ag on the more technologically significant Si(001) surface. In the Ag/Si(001) system, many ordered reconstructions (3×2 , 6×2 , and $2\sqrt{2} \times 2\sqrt{2}$) have been observed by growing Ag at elevated temperatures.^{10,12,13,27–30} However, at room temperature (RT), only two ordered phases, 2×1 and 2×2 , are known to form on Si(001), with the 2×1 phase being a disordered version of the 2×2 structure. What makes it possible for ordering to occur at RT is that the adsorbed species interacts weakly with the substrate and does not disrupt the substrate surface structure.

At RT, Ag/Si(001) is also a model system for the general behavior of the growth of a metal film in which adatoms do not interact strongly with the substrate. In such systems, alkali metals adsorb at different sites on the surface depending on the coverage, and the nature of the bonding between adatom and substrate was the matter of some dispute over a period of time.^{31,32} Group III and IV metal adatoms can order by adsorption in a particular bonding configuration on the surface.^{33–36} In contrast with the above, Ag on Si(001) is a unique case where in the 2×2 phase studied here, there is a balance between adatom–adatom interaction and adatom–substrate interaction to bring about an ordered phase. This

system also enhances the understanding of the general interaction between Ag and Si at solid interfaces, a subject that has attracted much interest from the fact that Ag(111) is an ideal substrate upon which to grow silicene.^{37–39}

RT growth of Ag on Si(001) follows the Stranski–Krastanov mode.^{9,11,14} Adsorbed Ag atoms aggregate to form a film up to one full monolayer, beyond which three-dimensional Ag islands are formed. What remains unclear, however, is the atomic structure of the initial Ag monolayer because previous scanning tunneling microscopy (STM) experiments at RT were often obscured by the high mobility of silver on Si(001).^{7,11,20} At RT, this film appears to have either a 2×1 or 2×2 structure with a high degree of disorder. Various models^{10,11,15,18} have been proposed where both the 2×1 and 2×2 structures are all based on a Ag dimer structure.

Here we present the atomic structure of the silver film grown on Si(001) at RT that challenges the notion of Ag dimers as the building block. Experiments using STM between 15 and 140 K succeeded in suppressing the mobility of silver on Si(001) and allow the identification of Ag tetramers in the silver film for the first time. This interpretation is supported by density functional theory (DFT) calculations of the Ag tetramer adsorption geometry, providing further insight into the surface bonding of silver adsorbed on Si(001).

In Figure 1, we contrast the STM images of the Ag films on Si(001) recorded at RT (on the left) with those recorded at 140 K (on the right). In all panels, as throughout this work, the Ag films were always prepared by depositing silver onto a clean

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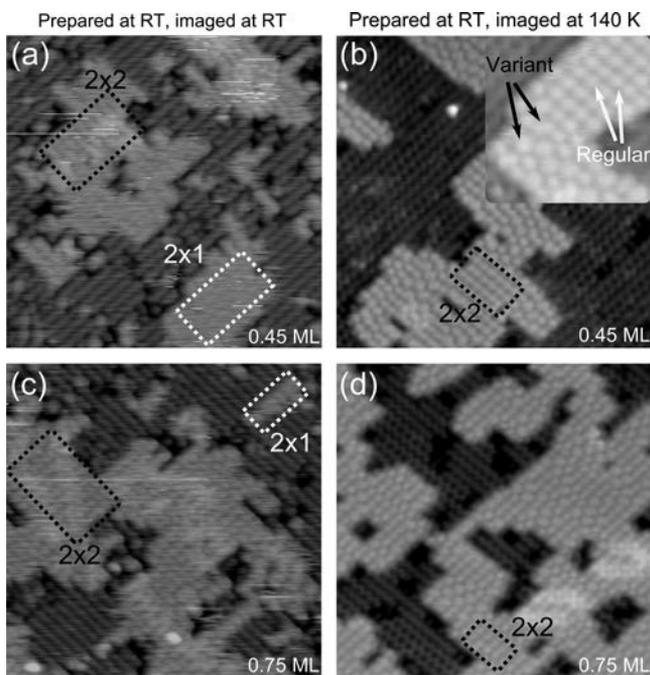


Figure 1. Filled-state STM images of Ag films on Si(001). In all panels, the Ag films were prepared by depositing silver on Si(001) held at RT and imaged at (a) RT, (b) 140 K, (c) RT, and (d) 140 K. All images are $250 \times 250 \text{ \AA}^2$ in size, recorded at -2.5 V with a tunnelling current of 20 pA . The inset in panel b is a closeup of the silver film, showing both regular and variant Ag tetramers.

Si(001) surface held at RT. The size and shape distributions of the formed patches of Ag film were found to be insensitive to imaging temperature.

Figure 1a,c shows representative STM images of the Ag films recorded at RT, corresponding to surface coverages of silver, Θ_{Ag} , of 0.45 and 0.75 ML, respectively. Both 2×1 and 2×2 periodicities are present inside the Ag films, with a relative increase of 2×2 over 2×1 as Θ_{Ag} increases. There are often fuzzy imaging streaks over the regions of the Ag film, indicative of the high mobility of Ag on Si(001) at RT. These observations are in good agreement with prior reports from this laboratory¹¹ and others.^{7,20,21}

Upon cooling to 140 K, the mobility of silver at the surface was greatly suppressed, thereby enabling better resolution of the interior structure of the Ag film, exemplified by Figure 1b,d. Clearly, the Ag film is composed of many ovals that occur once per 2×2 unit cell. We interpret these ovals as tetramers of silver based on the ratio of the number of Si atoms to the number of ovals, being $\sim 4:1$, for surface regions covered by Ag films. Because the atomistic density of the Ag film is identical to that of the Si(001) substrate,^{11,15–17} it follows that each oval consists of four Ag atoms and therefore is a Ag tetramer. Further evidence of this interpretation comes from DFT computations, as presented later in this paper.

On the basis of the surface alignment of Ag tetramers, we categorize them into the following two types, termed as “regular” and “variant”. As shown in the inset of Figure 1b, regular Ag tetramers are aligned in clear rows running perpendicular to the silicon dimer row direction, forming domains with 2×2 periodicity. By contrast, the “variant” Ag tetramers have a range of other alignments, often forming a disordered domain that separates 2×2 domains of regular Ag tetramers. Interconversions between regular and variant Ag

tetramers were occasionally observed at 140 K, suggesting similar stabilities on Si(001).

The adsorption sites of Ag tetramers are determined on the basis of the positions of the adjacent substrate Si atoms. In Figure 2, we show such an analysis, using a pair of STM images

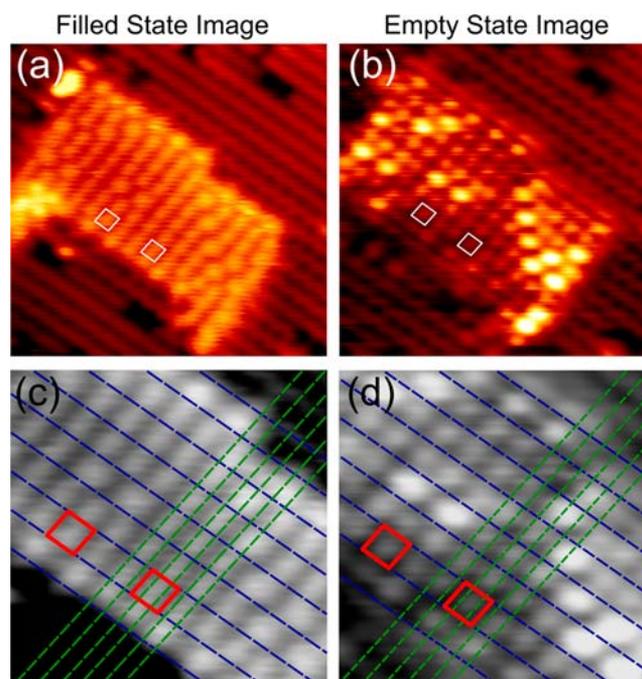


Figure 2. (a,b) Filled- and empty-state images of a Ag film on Si(001), respectively, recorded at 140 K. (c,d) Closeups of panels a and b overlaid in part by a mesh generated from the substrate to show the surface registry of the regular Ag tetramers. In panels c and d, the blue lines represent the center of the Si rows, whereas the green lines are aligned with the centers of Si dimers. Image parameters are as follows: (a) -3.0 V , 10 pA , $133 \times 133 \text{ \AA}^2$ in size; (b) $+3.9 \text{ V}$, 10 pA , $133 \times 133 \text{ \AA}^2$ in size; (c) -3.0 V , 10 pA , $75 \times 75 \text{ \AA}^2$ in size; and (d) $+3.9 \text{ V}$, 10 pA , $75 \times 75 \text{ \AA}^2$ in size. Boxes outline the same tetramers in all four panels.

of 0.15 ML Ag on Si(001) recorded at 140 K. Figure 2a,b shows filled-state and empty-state STM images of the same region; Figure 2c,d shows closeups of the images, with an overlaid mesh aligned with the neighboring uncovered Si substrate. The dashed blue lines represent the center of the Si dimer rows and are spaced $2a$ apart (where $a = 3.84 \text{ \AA}$, the length of one side of a single unit cell of the bulk terminated Si(001) surface), whereas the green dashed lines in the perpendicular direction are spaced $1a$ apart and are aligned with the centers of Si dimers in the clean areas flanking the Ag film. The white boxes in Figure 2a,b and the red boxes in Figure 2c,d enclose the same 2×2 unit. Additional images showing registration determination are shown in Figures S1 and S2 of the Supporting Information.

Note that in the empty-state images, the variant tetramers appear brighter than the regular tetramers and lie predominantly at boundaries between ordered domains of 2×2 regular tetramers. Because the positions of the variant tetramers can vary, the following analysis is focused on the regular tetramers.

In both images, the regular Ag tetramers are observed to center exclusively at the trough between two adjacent Si rows, with the long axis between two adjacent Si dimers of the same

Si row. This same registry is observed when examining all regular Ag tetramers in other STM images, recorded between 15 and 260 K, over the coverage range of 0.15 to 0.90 ML Ag on Si(001) and is further illustrated by the images in Figure 3.

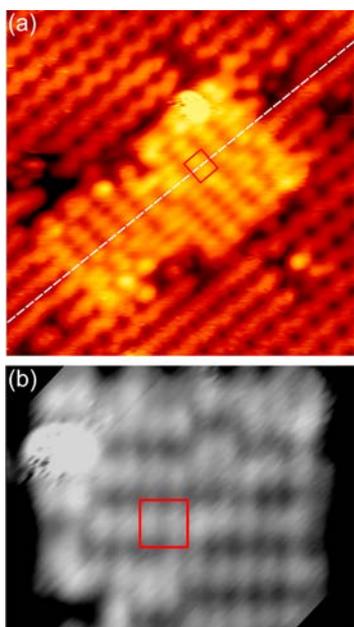


Figure 3. Filled-state image of 0.15 ML Ag on Si(001), recorded on a terrace at 65 K. (a) A patch of Ag film. (b) Enhanced view of the Ag film is presented and rotated to orient the Si dimer rows vertically. Red boxes enclose the same Ag tetramer. A nodal plane is visible, bisecting each Ag tetramer. Image parameters are as follows: (a) -2.3 V, 25 pA, $112 \times 12 \text{ \AA}^2$ in size and (b) -2.3 V, 25 pA, $55 \times 55 \text{ \AA}^2$ in size.

Figure 3 presents STM images that show a more detailed structure within each tetramer. As marked in Figure 3, each Ag tetramer exhibits a nodal plane in the middle of the usual STM maxima. Consequently, each Ag tetramer is composed of two ovals, with their long axes aligned along Si rows. A white dashed line demonstrates that the nodal plane lies along the trough of the Si dimer row. This imaging signature is of interest when comparing with the simulated STM images from DFT.

To gain further insight into the atomic structure, DFT calculations were carried out on the adsorption of 1 ML Ag on Si(001). As shown schematically in Figure 4a, the formation of Ag tetramers naturally occurred during structural optimization. In the optimized structure, the neighboring Ag atoms are separated by $\sim 2.8 \text{ \AA}$, in accordance with the experimental value of the nearest Ag–Ag separation of 2.84 to 2.94 \AA by ion scattering spectroscopy.¹⁵ This separation is larger than the typical Ag–Ag single-bond length of 2.53 \AA , as in the gaseous cluster of Ag₂,⁴⁰ but less than twice the van der Waals radius of a nonbonding Ag atom of 3.44 \AA .⁴¹ This is in the range of distance where argentophilic interactions⁴² are operative, accounting for the aggregation of four Ag atoms into a tetramer. Upon Ag adsorption, the Si dimers are no longer buckled, exhibiting an elongated Si–Si separation of 2.44 \AA compared with 2.36 \AA of a buckled Si dimer on clean Si(001). The Si–Ag separation is 2.44 \AA , which is about the covalent bond length of 2.45 to 2.60 \AA , as reported in the related system of Ag/Si(111).^{23,43,44} On the basis of these relaxed bond

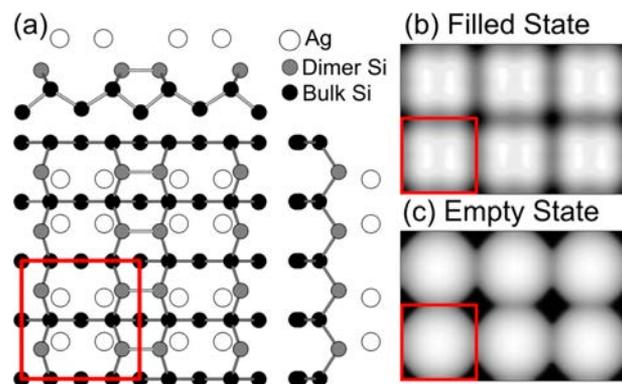


Figure 4. (a) Relaxed structure of 1 ML Ag on Si(001) shown in three projections. (b,c) Simulated filled-state (-1 V) and empty-state ($+1$ V) STM images, respectively. In each panel, a single Ag tetramer is enclosed by a red box.

distances, it is evident that both the tetramers in the Ag/Si(001) and the Ag trimers in the Ag/Si(111) system share a similar interaction with the Si layer underneath.

This optimized structure of adsorption is consistent with the following scenario of bonding: A Si dimer opens its π bond so that each Si atom covalently attaches to an adjacent Ag atom, in analogy to the adsorption of H atoms on Si(001).⁴⁵ The heat of adsorption per Ag atom was computed as 2.43 eV, in reasonable agreement with the experimental value of 2.55 eV at $\Theta_{\text{Ag}} = 1$ ML, as measured by single-crystal microcalorimetry.¹⁷

Furthermore, we simulated STM images using the structure optimized for 1 ML Ag on Si(001), as detailed above. Figure 4b,c presents the simulated images for both filled states and empty states, respectively. The surface registry of Ag tetramers, as observed in experiment, was successfully reproduced from our simulations. Indeed, the Ag tetramers were computed as a bright oval located in the Si trough, with the long axis between two adjacent Si dimers of the same Si row. Of particular note, the nodal plane of the Ag tetramer, shown in Figure 3, is present in the simulated filled-state image (Figure 4b). Two alternative models^{11,15} in the literature were also considered in our DFT computations. Simulations of these two models, however, failed to reproduce the surface registry, as derived from our STM measurements. Simulated STM images for these two models are shown in Figure S3 of the Supporting Information.

In summary, low-temperature STM and DFT calculations were employed to examine the structure of the silver film grown on Si(001) at room temperature. Upon cooling to below 140 K, STM imaging reveals that the silver film is composed of two kinds of tetramers, termed as regular and variant. The regular Ag tetramers are exclusively adsorbed at the trough between two adjacent Si rows, forming domains of a 2×2 periodicity. These experimental findings are in good agreement with the structure and simulated STM images obtained from DFT calculations.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.8b02746.

Experimental method, computation details, and additional results (PDF)

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Notes

The authors declare no competing financial interest.

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