

A structural model for silicotungstate (α - $\text{SiW}_{12}\text{O}_{40}^{4-}$) monolayers on silver (111)

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Abstract: Self-assembled monolayers of α - $\text{SiW}_{12}\text{O}_{40}^{4-}$ anions on Ag(111) surfaces adopt an ordered structure in which approximately square domains of anions separated by $10.2 \pm 0.5 \text{ \AA}$ are misoriented by about 30° relative to each other. An anion-substrate bonding model is proposed where α - $\text{SiW}_{12}\text{O}_{40}^{4-}$ anions act as tetradentate ligands bridging four silver surface atoms arranged at the vertices of $2 \times \sqrt{3}$ rectangle. The anions occupy translationally-equivalent bridging sites on a $\begin{pmatrix} 4 & 1 \\ 1 & 4 \end{pmatrix}$ Ag(111) superlattice whose primitive unit cell is almost square, with $a' = b = \sqrt{13} a = 10.42 \text{ \AA}$ and $\alpha = 92.2^\circ$.

The processing of oxide dielectric thin films on metal surfaces for microelectronic applications has received much attention in recent years. Two approaches in particular, sol-gel processing (ref. 1) and chemical vapor deposition (ref. 2) have proven to be effective routes to submicron films of crystalline dielectric oxides. These successes have raised the question whether methods might be developed for processing even thinner films of this type, namely, ultrathin films whose thickness is defined by molecular dimensions. Precedent for dielectric films of this type exists in the form of ultrathin organic films that are known as ordered molecular monolayers and multilayers (ref. 3). Ordered monolayers of organic thiolates on gold(111) surfaces, for example, are formed spontaneously upon immersion of Au(111) surfaces into solutions containing the corresponding thiol RSH (ref. 4). This self-assembly technique is quite versatile, and a wide variety of organic thiols are known to form self-assembled monolayers (SAM's) of this type (ref. 3).

We recently reported the self-assembly of silicotungstate ions α - $\text{SiW}_{12}\text{O}_{40}^{4-}$ on silver (111) surfaces (ref. 5). Immersion of Ag(111) surfaces into aqueous α - $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ solutions yielded ordered, adherent α - $\text{SiW}_{12}\text{O}_{40}^{4-}$ monolayers. According to *in situ* scanning tunneling microscopy (STM), the anions formed the approximately square adlattice shown in Figure 1 with an anion-anion separation of $10.2 \pm 0.5 \text{ \AA}$. The formation of these self-assembled inorganic monolayers opens up the possibility of engineering a variety of crystalline, ultrathin oxide films on metals for specific applications, given the large number of polyoxometallates that are known to be water-soluble (ref. 6). Engineering ultrathin oxide films on a molecular level requires moving beyond self-assembly techniques and attempting to control the assembly of polyoxoanions on metal surfaces. This in turn requires understanding the nature of anion-substrate bonding in these systems. Here we begin this task by proposing a model for structure and bonding in α - $\text{SiW}_{12}\text{O}_{40}^{4-}$ monolayers on Ag(111).

The silicotungstate anion α - $\text{SiW}_{12}\text{O}_{40}^{4-}$ has the so-called α -Keggin structure in which a tetrahedral oxoanion, here the orthosilicate anion SiO_4^{4-} , is encapsulated by an $\text{M}_{12}\text{O}_{36}$ cage, here a neutral $\text{W}_{12}\text{O}_{36}$ cage, in such a fashion that the tetrahedral symmetry of the central oxoanion is retained (ref. 7). It is therefore impossible for these silicotungstate anions to define a rigorously square lattice since the anions themselves do not have four-fold rotational symmetry. The anions do have four-fold roto-reflection symmetry, however, and when they are viewed along an $S_4(\bar{4})$ axis as in Figure 2a, they are seen to approximate square symmetry since the $S_4(\bar{4})$ symmetry operation becomes a $C_4(4)$ operation when the anion is projected onto a plane perpendicular to the S_4 axis. The anions therefore

can be placed on a square lattice as shown in Figure 2b. When each anion is brought into van der Waals contact ($d_{O...O} = 2.8 \text{ \AA}$) with each of its four nearest neighbors, a center-to-center anion-anion distance of 10.4 \AA is obtained, in good agreement with the $10.2 \pm 0.5 \text{ \AA}$ observed experimentally.

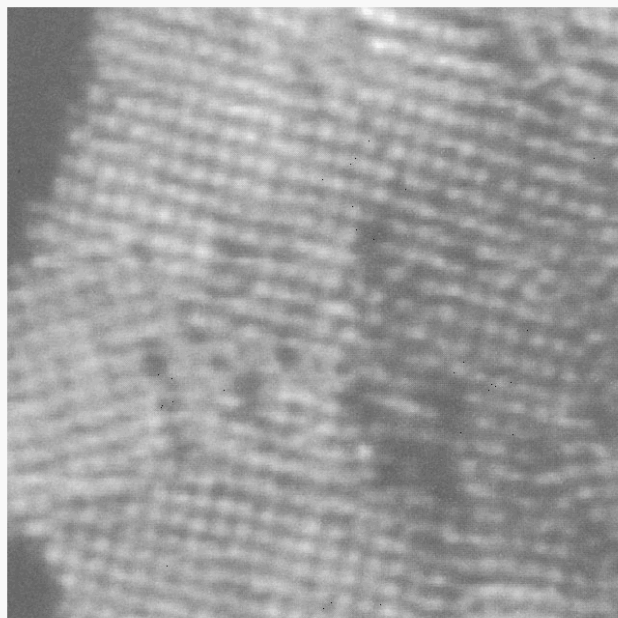


Fig. 1. $28 \times 28 \text{ nm}$ *in situ* STM image of an $\alpha\text{-SiW}_{12}\text{O}_{40}^{4-}$ monolayer on an Ag(111) surface in 0.1 M aqueous HClO_4 . [Reprinted with permission from *J. Am. Chem. Soc.* 1996, 118, 5812. Copyright 1996 American Chemical Society.]

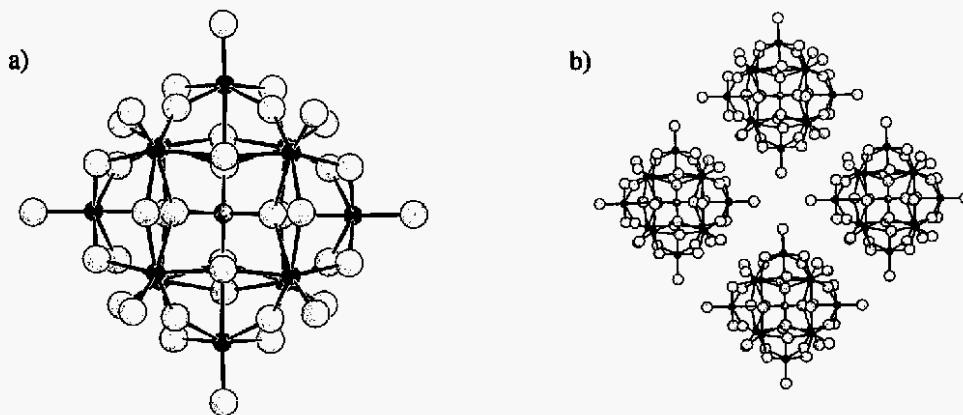


Fig. 2. Ball and stick model of (a) an individual $\text{SiW}_{12}\text{O}_{40}^{4-}$ anion and (b) a 2×2 square array of four $\text{SiW}_{12}\text{O}_{40}^{4-}$ anions. Tungsten atoms are represented by filled small circles, silicon atoms by small shaded circles, and oxygen atoms by large shaded circles.

The model shown in Figure 2b can account for the $\alpha\text{-SiW}_{12}\text{O}_{40}^{4-}$ adlattice on Ag(111) shown in Figure 1, but it cannot account for the domain structure also evident in Figure 1. The domains are oriented relative to each other by 30° , suggesting epitaxial growth of $\alpha\text{-SiW}_{12}\text{O}_{40}^{4-}$ adlattice on the hexagonal Ag(111) substrate. This epitaxy follows quite naturally from the silver surface-silicotungstate surface interaction implied by the anion adlattice structure shown in Figure 2b. In this structure, four oxygen atoms from each anion are in contact with the surface, and these four atoms are identified in Figure 3a where they are represented by filled circles. When this "footprint" is placed on the Ag(111) surface as shown in Figure 3b, it is seen to match closely the dimensions of a $2 \times \sqrt{3}$ silver atom rectangle. Using the known dimensions of the $\alpha\text{-SiW}_{12}\text{O}_{40}^{4-}$ anion (ref. 7) and the 2.89-\AA Ag(111) surface lattice spacing (ref. 8), the dimensions of the $\alpha\text{-SiW}_{12}\text{O}_{40}^{4-}$ footprint and the silver atom rectangle are 5.5×5.0

Å and 5.8×5.0 Å, respectively. In the language of coordination chemistry (ref. 9), the α - $\text{SiW}_{12}\text{O}_{40}^{4-}$ ion, when it acts as a tetradentate ligand, has the proper bite size to serve as a μ_4 -bridging ligand coordinated to four Ag(111) surface atoms defining a $2 \times \sqrt{3}$ rectangle.

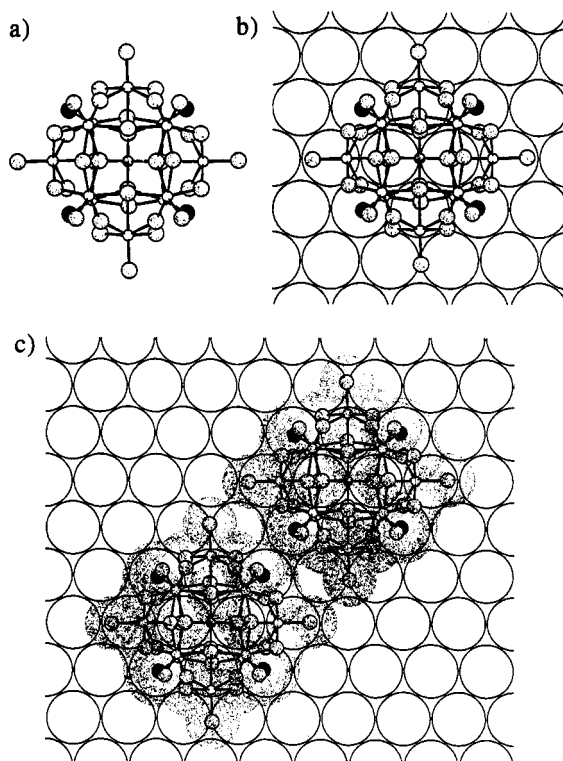


Fig. 3. (a) Ball and stick model of the α - $\text{SiW}_{12}\text{O}_{40}^{4-}$ anion drawn as in Fig. 2a but with the four oxygen atoms defining its "footprint" represented by filled large circles (see text). Ball and stick models of one and two $\text{SiW}_{12}\text{O}_{40}^{4-}$ adsorbed on an Ag(111) surface are shown in (b) and (c), respectively. Silicotungstate ions are represented as in (a), but shaded, 1.4-Å van der Waals spheres centered at the oxygen atoms are included in (c).

In order to form an epitaxial "square" adlattice on Ag(111), it is not sufficient that individual α - $\text{SiW}_{12}\text{O}_{40}^{4-}$ anions bind to the surface as shown in Figure 3b: each anion plus its four nearest neighbors must bind to the surface in the same fashion. As shown in Figure 3c, two α - $\text{SiW}_{12}\text{O}_{40}^{4-}$ anions can each occupy translationally-equivalent binding sites of the type shown in Figure 3b such that their center-to-center distance is $\sqrt{13} a = 10.42 \text{Å}$ Ag(111). In figure 3c, each oxygen atom is surrounded by shaded circle having a 1.4-Å van der Waals radius, and the anions are seen to be in close contact, with a shortest O...O separation of 2.9 Å. The structure shown in Figure 3b has C_{2v} (2m) point group symmetry and can accommodate four symmetry-equivalent nearest neighbors of the type shown in Figure 3c. As a result, an infinite array of α - $\text{SiW}_{12}\text{O}_{40}^{4-}$ anions can be constructed on Ag(111) using only this nearest-neighbor relationship. A primitive unit cell for this array can be obtained directly from the set of four adsorbed anions shown in Figure 4a. This primitive cell, shown in Figure 4b, is almost square, with $\sqrt{13} a = 10.42\text{-Å}$ unit cell axes intersecting at 92.2° , and is described by $\begin{pmatrix} 4 & 1 \\ 1 & 4 \end{pmatrix}$ in standard matrix notation. The conventional centered cell shown in Figure 4c is rigorously rectangular ($a' = 5a = 14.45 \text{Å}$ and $b' = 3\sqrt{3} a = 15.02 \text{Å}$ with $c2mm$ plane group symmetry. Formation of this $c2mm$ superstructure on the $p6mm$ Ag(111) substrate lattice involves a reduction in point group symmetry from C_{6v} (6mm) to C_{2v} (2mm). Since C_{2v} is a subgroup of C_{6v} and the order of C_{6v} (12) is three times that of C_{2v} (4), three twin domains are possible for the $c2mm$ Ag(111) - $\begin{pmatrix} 4 & 1 \\ 1 & 4 \end{pmatrix}$ - $\text{SiW}_{12}\text{O}_{40}^{4-}$ surface compound. Only two of these three possibilities are observed in Figure 1.

The nearest-neighbor relationship between $\alpha\text{-SiW}_{12}\text{O}_{40}^{4-}$ anions shown in Figure 3 is only one of many possibilities involving the anion-substrate interaction shown in Figure 3b, and it is not even the shortest nearest-neighbor relationship possible. As a result, several different surface compounds can be envisioned. Close examination of STM images of $\alpha\text{-SiW}_{12}\text{O}_{40}^{4-}$ anions on Ag(111) obtained at low surface coverage (ref. 5) has revealed adlattice structures where $\alpha\text{-SiW}_{12}\text{O}_{40}^{4-}$ anions are less densely packed than in the $c2mm$ structure described above. We are currently characterizing these new surface phases in terms of the bonding model described above.

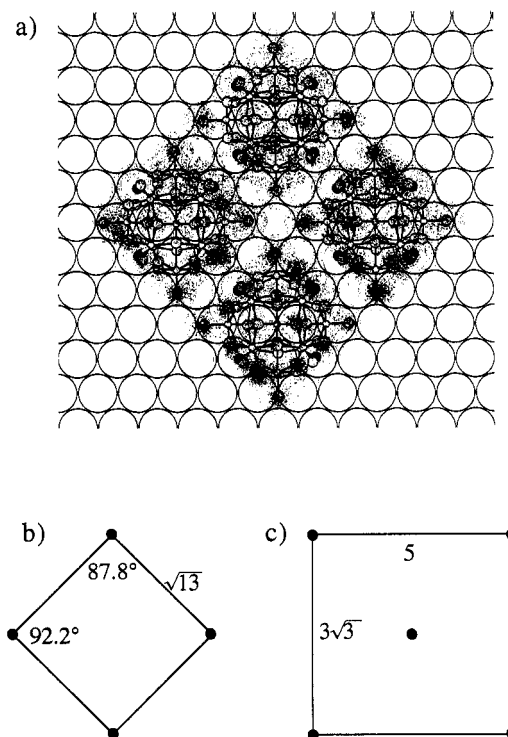


Fig. 4. A 2×2 fragment of the proposed $\text{Ag}(111) - \begin{pmatrix} 4 & 1 \\ 1 & 4 \end{pmatrix} - \text{SiW}_{12}\text{O}_{40}^{4-}$ structure is shown in (a), where atoms are labeled as in Fig. 3c. Primitive and centered unit cells for this structure are shown in (b) and (c), respectively.

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