Non-equilibrium growth of metal clusters on a layered material: Cu on MoS$_2$

Dapeng Jing$^{1,7}$, Ann Lii-Rosales$^{1,3,7,8}$, King C Lai$^{1,4}$, Qiang Li$^5$, Jaeyoun Kim$^5$, Michael C Tringides$^{1,4}$, James W Evans$^{1,4}$ and Patricia A Thiel$^{1,3,6,9}$

1 Ames Laboratory, Ames, IA 50011, United States of America
2 Materials Analysis and Research Laboratory, Iowa State University, Ames, IA 50011, United States of America
3 Department of Chemistry, Iowa State University, Ames, IA 50011, United States of America
4 Department of Physics and Astronomy, Iowa State University, Ames, IA 50011, United States of America
5 Department of Electrical and Computer Engineering, Iowa State University, Ames, IA 50011, United States of America
6 Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011, United States of America
7 These authors contributed equally.
8 Current address: Department of Chemistry, University of Colorado Boulder, Boulder, CO 80309, USA.
9 Author to whom any correspondence should be addressed.
E-mail: pthiel@ameslab.gov

Keywords: scanning tunneling microscopy, MoS$_2$, growth shape, copper

Abstract

We use a variety of experimental techniques to characterize Cu clusters on bulk MoS$_2$ formed via physical vapor deposition of Cu in ultrahigh vacuum, at temperatures ranging from 300 K to 900 K. We find that large facetted clusters grow at elevated temperatures, using high Cu exposures. The cluster size distribution is bimodal, and under some conditions, large clusters are surrounded by a denuded zone. We propose that defect-mediated nucleation, and coarsening during deposition, are both operative in this system. At 780 K, a surprising type of facetted cluster emerges, and at 900 K this type predominates: pyramidal clusters with a triangular base, exposing (311) planes as side facets. This is a growth shape, rather than an equilibrium shape.

1. Introduction

Cu is a material of choice for microelectronic interconnects due to its low resistivity [1]. However, this advantage can be nullified by surface scattering of electrons, which increases the electrical resistivity of Cu when Cu film thickness drops below about 40 nm for most substrates. This currently limits the ability to shrink Cu interconnects below this thickness [2]. Recently, the possibility has emerged of using two-dimensional (2D) materials, such as transition metal dichalcogenides and graphene, as interfacial layers at Cu interconnects. In particular, Shen et al have shown that Cu films interfaced with MoS$_2$ show much improved conductivity in the low-thickness regime, because scattering is reduced at the interface [3]. At the same time, ultrathin physical barriers that impede Cu diffusion into dielectrics without increasing the resistivity of the interconnect itself are highly desirable [4, 5]. MoS$_2$ is also promising for that purpose, making it a potential multifunctional component [3, 6].

The interaction of MoS$_2$ with Cu is also important from the perspective of magnetic properties, where the ability to induce and manipulate magnetic states in MoS$_2$ opens the door to spintronics applications. Here, Xia et al [7] have shown that MoS$_2$ layers doped with Cu ions are ferromagnetic and display a high Curie temperature, which is rather surprising given that Cu is non-magnetic, but is in accord with earlier theoretical predictions [8, 9]. Other areas where the combination of Cu and MoS$_2$ shows promise are tribology (enhanced wear resistance) [10, 11], and electrocatalysis (hydrogen evolution reaction) [12].

A previous experimental study of the interaction between Cu and MoS$_2$ focused on using sulfur-impregnated bulk Cu as a substrate for growth of MoS$_2$ [13]. That study demonstrated the ability to
grow large, well-ordered, monolayer islands of MoS2. In this paper, we take the opposite approach and use the (0001) surface of bulk MoS2 as a substrate for growth of Cu. We include data from depositions carried out at high deposition temperature ($T_{\text{dep}}$) of 600–900 K, and high exposures. We find that these conditions produce surprisingly large, numerous, and faceted Cu structures. One such faceted structure is particularly unexpected—a triangular pyramid with unanticipated side facets which are not low-index Cu crystal planes. We propose that this structure forms because it has a particularly good epitaxial match with the substrate.

Elsewhere, we report a comprehensive study in which density functional theory (DFT) is used to analyze adsorption, intercalation, diffusion, and adhesion in this system [14]. In the present paper, we draw upon some of those DFT results. Specifically, the adsorption energy of a Cu atom is used to estimate its residence time before desorption; the lower limit of the diffusion barrier is used to estimate the distance that an atom can travel during its residence; and the adhesion energy between Cu(111) and MoS2(0001), together with Cu surface energies, is used to determine the equilibrium crystal shape of a supported Cu nanoparticle.

This paper is organized as follows. Experimental methods and MoS2 sample characterization are described briefly in section 2, with further details available in the supplemental information (SI). Experimental results are presented in section 3. A discussion and concluding remarks comprise sections 4 and 5, respectively.

2. Experimental methods and MoS2 sample characterization

All Cu depositions, and all subsequent XPS and STM experiments, were carried out in a single Omicron ultrahigh vacuum (UHV) chamber. Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and atomic force microscopy (AFM) experiments were carried out after the sample was prepared in UHV and transferred to the appropriate instrument in air. Details of the instrumentation, sample preparation, and analysis procedures are given in the SI. Here we provide some of the most pertinent and unique details.

The MoS2 (molybdenite) specimens were naturally-occurring shards purchased from SPI Supplies, about 0.5 mm thick. They were cut with scissors into smaller pieces, each with an area of approximately 8 mm × 8 mm, suitable for mounting on the UHV sample stage. When each sample was first used, it was outgassed in UHV at 625 K for several hours. Prior to each subsequent experiment, the sample surface was regenerared by cleavage with Scotch tape in air, and then re-placed in the UHV chamber, where it was outgassed at 625 K for 20 min. Neither XPS nor EDS showed any detectable impurities on the MoS2 surface after this treatment. Results from x-ray diffraction (XRD) of the MoS2 sample are consistent with the expected 2H phase, both initially and after Cu deposition at 900 K, although the co-existence of the 3R phase cannot be completely ruled out. XPS also showed no detectable loss of sulfur from clean MoS2 upon heating, even to 900 K, consistent with earlier reports on the thermal stability of bulk MoS2 [15, 16]. Upon heating, the core levels underwent a rigid shift to lower binding energy (BE), which has been previously attributed to the generation of defect states in the band gap [16]. The XPS, EDS, and XRD data are provided in the SI. In summary, annealing to 900 K does not induce chemical state or stoichiometry change in bulk MoS2.

This paper shows data from different samples, acquired with different instruments. Orientations of features, particularly pyramidal clusters, cannot be compared across images.

Cu was deposited from a Mantis QUAD-EV-C Mini e-beam evaporator, typically operated at 31–34 watts (accelerating voltage 2 kV). This resulted in a flux of 11 ± 1 monolayers (ML) of Cu per minute, equivalent to 2.3 ± 0.2 nm min$^{-1}$, based on analysis of Cu coverage after fixed deposition time at 300 K. (Here, one Cu ML is assigned the density of Cu atoms in a (111) plane of bulk Cu.) Most Cu depositions lasted either 30 s corresponding to integrated flux or exposure ($\varepsilon$) of 5.5 ± 0.5 ML, or 25 min corresponding to $\varepsilon = 280 ± 30$ ML.

3. Experimental results

3.1. Clean MoS2 surface

MoS2 is comprised of S–Mo–S trilayers (TLs) in which atoms are bound by covalent-ionic bonds, and trilayers are bound to each other by van der Waals forces. In each TL, a Mo monolayer is bracketed by S monolayers. The (0001) surface of MoS2 thus presents an S monolayer at the top of a TL. Figure 1(a) shows an STM image of the initial clean surface, where the dark spots correspond to defects, which generally have widths of 2–4 nm at the top rim, and depths of 1–2 TLs. The density of all defects is $(6.0 ± 0.1) \times 10^3 \mu m^{-2}$ in this experiment. However, in another experiment some regions of the surface exhibit...
Figure 1. Topographic STM images of clean MoS$_2$, and of MoS$_2$ after Cu deposition at 300 K. (a) Clean MoS$_2$. Dark spots are defects. Tunneling conditions are: $V_{\text{tip}} = 0.25$ V, $I = 0.33$ nA. (b, c) STM images obtained at different magnifications, following deposition of Cu at 300 K with $\varepsilon = 5.5$ Cu ML. Tunneling conditions are: $V_{\text{tip}} = -2.1$ V, $I = 0.26$ nA. (d, e) STM images from a separate experiment at $T_{\text{dep}} = 300$ K, under conditions nominally identical to (b, c), except tunneling conditions are $V_{\text{tip}} = -2.0$ V, $I = 0.17$ nA. The white oval in (d) highlights two clusters that have apparently merged. The diagonal stripes in (e) are noise. (c’ and e’) Profiles corresponding to horizontal lines in panels (c) and (e), respectively. Blue profiles are displaced vertically for clarity.

Table 1. Summary of densities, sizes, and shapes of major features observed in SEM and STM. Widths are approximate. The phrase 'polyhedron-like' means that in the SEM images, some clusters resemble regular polyhedra such as octahedra or prisms. For comparison, the density of defects on the clean MoS$_2$ surface is $6 \times 10^3 \, \mu$m$^{-2}$.

| $T_{\text{dep}}$ | $N_{\text{al}}$ ($\mu$m$^{-2}$) | Width (nm) | Shape descriptions |
|-----------------|-----------------|------------|------------------|
| 300 K           | $2.7 \pm 0.31 \times 10^3$ | 10–40      | Slightly round-top, with hexagonal + triangular footprints |
| 625 K           | 13 ± 0.5        | 100–500    | Irregular faceted + rounded |
| 700 K           | 2.6 ± 0.1       | 200–500    | Irregular faceted + rounded |
| 780 K           | 0.50            | Large clusters: 100–1000 | Large clusters: irregular faceted + polyhedron-like + rounded (rare) |
| 2.8             | 2.8             | Small clusters: 50–300 | Small clusters: pyramidal |
| 900 K           | 0.08 ± 0.01     | 1000–3000  | Pyramidal + truncated pyramidal + other polyhedron-like |

significantly lower defect density. Elsewhere, Addou et al [17] showed a similar density of defects (in their figure 1(a)) immediately after exfoliation of naturally-occurring bulk MoS$_2$, without heating, though they also reported heterogeneity in defect distribution. We believe that a density of $6 \times 10^3 \, \mu$m$^{-2}$ is representative of the majority of the surface and we use this value going forward. As noted in section 2, annealing at 900 K does not induce structural, chemical state or stoichiometry change in these bulk MoS$_2$ samples.

3.2. Morphology of Cu films from 300 to 900 K

When Cu is deposited on the MoS$_2$ surface at $T_{\text{dep}} = 300$ K for 30 s (figures 1(b)–(f)), it forms a dense array of islands that are roughly 10 to 40 nm wide and 1.5 to 4 nm tall; hence these islands are rather flat or quasi-2D. Many exhibit triangular or hexagonal footprints and slightly rounded tops. The island density is about half that of defects (table 1), indicating that nucleation is heterogeneous at $T_{\text{dep}} = 300$ K. The island density may be diminished somewhat by growth coalescence; some shapes, such as the one encircled in figure 1(e), reveal that merging has occurred.

Deposition at 625 K for a much longer time, 25 min, produces many clusters with irregular shapes (figures 2(a)–(c)). While facets are often visible, the overall shapes are usually irregular or rounded. The density is at least two orders of magnitude smaller, $13 \pm 0.5 \, \mu$m$^{-2}$, than for deposition at 300 K. This
Figure 2. SEM images of Cu clusters on MoS$_2$, at different magnifications and different $T_{\text{dep}}$, with $\varepsilon = 280$ Cu ML. Imaging mode is secondary electrons in all panels except (g), (i), and (l), where backscattered electrons are collected. Note that the image in panel (l) comes from a different deposition experiment than (j, k), but conditions are nominally identical. The arrow in (h) points to a large cluster surrounded by a denuded zone. The head of the arrow is directly below a polyhedron-like (specifically, octagon-like) cluster. Inset in (h) magnifies a region containing only pyramidal clusters. Ovals in (i) highlight regions of fivefold symmetry (twinning).

suggests coarsening during deposition and/or a drop in the number of active nucleation sites at elevated $T_{\text{dep}}$.

As the deposition temperature increases (figure 2) at constant deposition time, the size of the largest Cu clusters increases and density falls further. This is evident by comparing the SEM images at lowest magnification, i.e. the images in the left-hand column of figure 2. Sizes and densities are compiled in table 1. Cluster shapes go from being rounded, or facetted but irregular, to resembling regular polyhedra. This progression in shapes is evident by comparing the SEM images at highest magnification, i.e. the images in the right-hand column of figure 2. Twinning (manifest as local five-fold symmetry [18, 19]) is common in the lower range of $T_{\text{dep}}$, but rare at 900 K.

One type of polyhedron-like shape—the pyramidal shape with a triangular base—emerges as small clusters at 780 K, where it coexists with much larger, irregular polyhedral shapes (figure 2(h)). The pyramids (including truncated pyramids) become dominant and large at 900 K (figures 2(j)–(l)). The area histogram in figure 3(c), for $T_{\text{dep}} = 780$ K, shows the small pyramidal clusters exist in a separate peak from the large clusters. (Actually, there are separate populations for lower $T_{\text{dep}}$ as well, as shown in figures 3(a) and (b).) This bimodal distribution of cluster sizes may originate from coarsening during deposition, with small clusters reflecting direct nucleation and growth, and larger clusters reflecting coarsening. This is discussed more fully in section 4.

The spatial distributions of small pyramidal clusters at 780 K are strikingly heterogeneous. As shown in figure 2(h), there are often denuded zones surrounding the large clusters, while the pyramidal clusters group in regions that are more distant from large clusters. This also suggests that the pyramidal clusters...
Figure 3. Cluster area distributions from SEM images such as those in figure 2, at different $T_{\text{dep}}$: (a) 625 K; (b) 700 K; (c) 780 K. In each pair of panels, the top histogram shows a fine bin size $= 6.84 \times 10^{-5} \mu m^2$ at cluster areas up to 0.02 $\mu m^2$, which reveals the structure in the histogram best for small cluster areas. The bottom panel shows a coarser bin size $= 2.05 \times 10^{-2} \mu m^2$ at cluster areas up to 1.0 $\mu m^2$, which reveals structure better for large cluster areas. In the bottom panel of (c), counts at cluster areas below 0.08 $\mu m^2$ are truncated to facilitate viewing the higher area range.

nearby large islands are consumed by coarsening. The following subsection analyzes the shapes of these pyramids.

3.3. Shapes of the pyramids
We assume that the base of each pyramid is a (111) plane of fcc Cu, related to the underlying MoS$_2$ by a $(5 \times 5)$Cu(111)/(4 × 4)2H-MoS$_2$(0001) coincidence lattice. This is the same as the interface structure proposed by Kim et al. in their study of MoS$_2$ on Cu [13]. It is supported by their observation of a moiré pattern with the expected periodicity [13]. In this structure, the Cu lattice is strained by only a small amount: $-1.1\%$ based on lattice constants in the literature, or by $+0.4\%$ to $-0.6\%$ based on lattice constants from DFT, depending on the configuration of Cu used as the reference point [20]. An obvious possibility is that the sides of the pyramids are also (111) planes, which would make the pyramids tetrahedral.

The 3D shapes of the pyramids are shown in figure 4, measured by using both STM and AFM. For comparison, the idealized geometry of a tetrahedral pyramid (i.e. a pyramid with (111) planes as side facets) is shown in figure 4(a). It can be seen that a profile through points BAE would trace out an asymmetric shape with angles of 55$^\circ$ and 71$^\circ$ at the base (figure 4(b)). However, the angles measured for the Cu/MoS$_2$ pyramids deviate strongly from these tetrahedral angles. For instance, at $T_{\text{dep}} = 900$ K the average smaller angle is $\alpha_{\text{sm}} = 15.7^\circ \pm 0.5^\circ$, and $\alpha_{\text{lg}} = 28.5^\circ \pm 1.4^\circ$. In fact, these measured angles agree well with ideal angles if the three side facets are (311) planes, in which case $\alpha_{\text{sm}} = 15.8^\circ$ and $\alpha_{\text{lg}} = 29.5^\circ$. Line profiles drawn along the other two edges of pyramids such as those in figures 4(e) and (g) confirm that all three faces are (311) planes.

We have also considered possible geometries in which the base remains a (111) plane, but the three side facets are other low-index planes with reasonably low surface energies: (221), (331), or (100). All can be ruled out on the basis of the measured angles, as shown in the SI. Only the (311) plane is compatible with the experimental data.

The clusters in figure 4 span more than an order of magnitude in size—from a width of 0.2 $\mu m$ in figure 4(c) to 3 $\mu m$ in figure 4(g). Comparison indicates that as they become larger, pyramids become more perfect—their profiles become smoother, horizontal edges become more linear, and side facets become better aligned with (311) planes.

In all cases, the side of the profile associated with the smaller angle has a near-vertical base. Sometimes the other side does as well. This may reflect an overhang on the side of the pyramid, creating an empty space that is impenetrable with a conventional scanning probe. The near-vertical portion of the profile would then represent the contour of the side of the tip as it touches and rises above the overhang, appearing near-vertical on the length scales of these profiles.

3.4. Comparison with equilibrium crystal shape
The pyramidal shape can be compared with the equilibrium crystal shape of Cu on MoS$_2$. Assuming (as above) that the cluster’s base is an fcc(111) facet, the equilibrium shape is determined by a Winterbottom analysis [21] (also attributed to Kaishew [22, 23]) which takes the unsupported fcc Cu Wulff shape and
Figure 4. Shapes of pyramidal clusters. (a) Ideal shape of a tetrahedron, with BCD as the base and blue triangle BAE drawn as a cross-section. (b) Ideal profile of a tetrahedron, defined by the blue triangle in panel (a). (c) STM topographic image of a pyramidal island, prepared at $T_{\text{dep}} = 780$ K and $\varepsilon = 5.5$ Cu ML. Inset shows a semi-3D perspective. Tunneling conditions are $V_{\text{tip}} = +0.55$ V and $I = 0.9$ nA. (d) Profile along the straight line in panel (c). (e) AFM topographic image of a pyramidal island, prepared at $T_{\text{dep}} = 780$ K and $\varepsilon = 280$ Cu ML. Inset shows a semi-3D perspective. (f) Profile along the straight line in panel (e). (g) AFM topographic image of a pyramidal island, prepared at $T_{\text{dep}} = 900$ K and $\varepsilon = 280$ Cu ML. Inset shows a semi-3D perspective. (h) Profile along the straight line in panel (g).

Figure 5. Schematics of an equilibrated Cu cluster supported on MoS$_2$. (a) Top view. (b) Side view. In both panels, blue indicates the Cu cluster above the MoS$_2$ substrate, and red indicates the region of the freestanding cluster that is truncated in the Winterbottom construction. Darker shades indicate facets with higher (less-favorable) $\gamma$. The extent of truncation is determined by the adhesion energy ($\beta$) between Cu(111) and MoS$_2$(0001), and the surface energy ($\gamma$) of Cu(111), $\gamma_{111}$. The procedure is described more fully elsewhere [20, 24]. We use the value $\beta = 0.874$ J m$^{-2}$ calculated with the van der Waals density functional (vdW-DF) known as vdW-DF2-B86R [14, 25], for the above-mentioned $(5 \times 5)$Cu(111)/(4 $\times$ 4)2h-MoS$_2$(0001) coincidence lattice. Values of $\gamma_{111}$ and $\gamma$’s for the six other most-favorable low-index surfaces of fcc Cu, are available from DFT, calculated with the Perdew–Burke–Ernzerhof (PBE) functional [26]. The ratio of cohesive energies of a bulk Cu atom with vdW-DF2-B86R to PBE functional is 1.04. To make these $\gamma$ values more consistent with $\beta$, we use this ratio to rescale them. The result is the shape shown in figure 5, where blue denotes the actual supported cluster and red denotes the truncated region. The aspect ratio (width:height) of the supported cluster is 1.7, which is much smaller than the aspect ratio of the pyramids (≈4 from figure 4(h)). This demonstrates that the pyramids are far from equilibrated. Figure 5 also indicates the different facets present in the equilibrium shape, including the (311) facets (which make only a minor contribution to the total area). The top facet of the equilibrium shape is a flat, hexagonal (111) face. This provides additional strong evidence that the pyramids, with their pointed tops, are not equilibrated. Hence, pyramids must result from growth kinetics, i.e. they represent a growth shape (and the same is true of the irregular clusters).
3.5. Chemical state of Cu
The chemical state of Cu can be difficult to determine from XPS alone due to negligible chemical shifts in some Cu compounds, but it can be assessed by combining Auger and XPS data in a Wagner plot [27], which is a graphical display of the kinetic energy (KE) of the sharpest Auger line versus the BE of the most intense photoelectron line. Figure 6 shows a Wagner plot that includes known compounds of Cu, plus our experimental data for $T_{\text{dep}} = 300$ K and 900 K. The experimental data points are very close to the reference point for metallic Cu. They are well separated from the reference points for a selection of other Cu compounds, including copper sulfides. This analysis shows that Cu exists in the metallic state when $300 \text{ K} \leq T_{\text{dep}} \leq 900$ K. Elemental mapping by EDS (shown in SI), reveals that the clusters are pure Cu and the regions between them are pure MoS$_2$, i.e. there is no elemental intermixing. Both types of data indicate there is no chemical reaction of Cu with MoS$_2$ at the deposition temperatures of interest.

3.6. Effect of $T_{\text{dep}}$ on coverage
XPS data provides further information about the effect of $T_{\text{dep}}$. Figure 7 shows the Cu 2p XPS peak intensity as a function of increasing $T_{\text{dep}}$. The data are obtained after short Cu depositions, with one exception as noted in the caption. The Cu 2p$_{3/2}$ BE occurs at $932.9 \pm 0.1$ eV and is invariant with temperature, as is the peak shape and full-width at half-maximum (FWHM).

The Cu XPS intensity is determined by a convolution of Cu coverage and Cu morphology, both of which can change with temperature, e.g. due to desorption or coarsening [28]. Nonetheless, it can be safely concluded from the data in figure 7 that the amount of Cu on the surface decreases with increasing temperature, reaching low values at 700 K, after short depositions. This is due to desorption of Cu. In support, our DFT shows that the adsorption energy of a single Cu atom at the most favorable site on MoS$_2$ is 1.485 eV [14], which corresponds to a residence time on the order of $10^{-2}$ s at 700 K. This is discussed more fully in section 4.

The conclusion that desorption is rapid at 700 K may seem to contradict observations of large faceted Cu clusters on the MoS$_2$ surface following deposition at this temperature and above. However, it is important to note that these XPS data were obtained after short deposition times where the Cu atoms primarily interact with clean MoS$_2$. In section 5, we will argue that once Cu clusters nucleate, they serve as stable traps for incident Cu atoms, leading to large Cu clusters after long deposition times. In other words,
Table 2. Estimated adsorption lifetime \( \tau \), and RMS diffusion length \( \lambda_\tau \), calculated from \( E_{\text{ads}} = -1.485 \text{ eV} \) and \( E_{\text{diff}} = 0.143 \text{ eV} \) [14], for different \( T_{\text{dep}} \). Values are given to one significant figure. The calculations assume a common prefactor of \( 10^{12.5} \text{ s}^{-1} \) for desorption and diffusion. For comparison, an approximate characteristic length, \( L \), between Cu islands is derived from the SEM-based densities \( N_{\text{isl}} \) in table 1 using \( L = N_{\text{isl}}^{-1/2} \).

| \( T_{\text{dep}} \) (K) | \( \tau \) (s) | \( \lambda_\tau \) (\( \mu \)m) | \( L \) (\( \mu \)m) |
|---|---|---|---|
| 625 | \( 3 \times 10^{-1} \) | 200 | 0.3 |
| 700 | \( 2 \times 10^{-2} \) | 50 | 0.6 |
| 900 | \( 7 \times 10^{-5} \) | 4 | 4 |

the condensation coefficient [29] is initially small, but increases with increasing Cu coverage. This is why long deposition times (high \( \varepsilon \)) are necessary at high \( T_{\text{dep}} \).

4. Discussion

This paper mainly reports empirical observations of Cu growth on MoS\(_2\), some of which are quite surprising. The observation of large, faceted Cu clusters after growth at high temperatures might be anticipated given behavior in other metal heteroepitaxial growth systems [30, 31], but the development of pyramidal clusters with (311) side facets is unexpected. Other important observations are the bimodal size distributions, denuded zones around large clusters, and evidence of a low condensation coefficient at growth temperatures. This section includes speculation about phenomena that may underlie and link the experimental observations. However, growth is undoubtedly governed by a complex and interrelated set of processes (adsorption, desorption, diffusion of various types, nucleation, cluster reorganization, coarsening). Quantitative modeling is a major project, deferred to future work.

4.1. Role of Cu desorption from the MoS\(_2\) surface

The faceted clusters form under conditions where there is rapid desorption of atomic Cu from the MoS\(_2\) surface, based both on XPS and on DFT. Rapid desorption of Cu from MoS\(_2\) above 600 K is also supported by calculations of the adsorption lifetime, \( \tau \), based on the adsorption energy of \(-1.485 \text{ eV} \) [14] and assuming a pre-exponential factor of \( 10^{12.5} \text{ s}^{-1} \). Some values are tabulated in table 2, showing that \( \tau \) is very short (well below 1 s) above 600 K. Nonetheless, Cu clusters form because after some Cu islands nucleate, they grow and become traps for impinging or diffusing Cu atoms; Cu incorporated in these clusters is stable against desorption, which begins around 900 K for Cu on Cu [28, 32]. Hence, in the limit of zero Cu coverage, where the dynamics are limited by the interaction of Cu with clean MoS\(_2\), the coverage of Cu is very low. However, a few Cu clusters nucleate and as they do, the condensation coefficient of Cu increases, leading eventually to the development of large clusters shown in figure 2.

To test this picture, we have calculated the root-mean-square (RMS) diffusion length \( \lambda_\tau = 2(D\tau)^{1/2} \), where \( D \) is the diffusion coefficient, from DFT energies [14]. The diffusion barrier being used to calculate \( \lambda_\tau \) is an approximation to the true barrier [14], and real values of \( \lambda_\tau \) may be somewhat shorter. The results are shown in table 2, which includes characteristic separations between Cu clusters obtained from experiment. It is clear that even though adsorption lifetimes are short, the lifetimes are still long enough for the diffusing Cu atoms to reach a nearby existing Cu cluster on the MoS\(_2\) surface, before desorption.

4.2. Defects and coarsening

At 300 K, the correspondence between defect density and cluster density strongly suggests that nucleation is heterogeneous. As temperature increases, cluster density falls. This could be due to a decrease in the number of defects that are active for nucleation, or the onset of coarsening during deposition, or both. Coarsening can account for other features of the data as well: denuded zones around large clusters at 780 K (figure 2(h)), and bimodal distributions of island sizes (figure 3; also see below). It is interesting that at 625 K and 700 K, cluster separations \( L \) are much shorter than the estimated diffusion length \( \lambda_\tau \) (table 2). In this context, it is appropriate to note that a common feature of ‘incomplete condensation’ (island formation during deposition in the presence of limited desorption) either for homogeneous or heterogeneous nucleation is that condensation starts off as incomplete (where the cluster separation, \( L \), is above \( \lambda_\tau \)) and ends up as complete (when \( L \) has dropped below \( \lambda_\tau \)) [29]. In this system presumably heterogeneous nucleation dominates, but the number of defects that act as effective nucleation centers must be decreasing with \( T_{\text{dep}} \). Overall, it appears that both coarsening and defect-mediated nucleation are important in this system.

There is precedent for bimodal size distributions in other growth systems, including metal/metal such as Co/Cu(100) [33, 34], metal/oxide such as Pd/MgO [35], and quantum dots such as InAs/InP [36]. Bimodal
distributions are generally attributed to the existence of competing pathways for island nucleation and/or growth. In the case of Co/Cu(100), for instance, the two pathways are place-exchange-mediated nucleation (replacement of Cu by Co in the substrate), and homogeneous nucleation of Co atoms [33, 34]. The former tends to produce a large population of small islands, whereas the latter tends to produce a narrower monomodal distribution of large islands [37]. In the case of InAs/InP, the bimodal distribution is attributed to the abrupt appearance of 3D islands from a wetting layer, as is usual in Stranski–Krastanov growth, vs continuous evolution of small features into well-developed 3D islands [36]. In the Pd/MgO system, the small islands were originally attributed to secondary nucleation, although no evidence was provided that the small islands formed after the large islands [35]. In our case, and possibly in the Pd/MgO system, the bimodal distribution can be attributed to a combination of defect-mediated nucleation and post-nucleation coarsening. The many defects provide traps for deposited Cu atoms, and thus sites for heterogeneous nucleation. Clusters growing at such defects would have a monomodal distribution of sizes corresponding to a distribution of capture zone areas for the various defects [38, 39]. However, especially at higher T_{dep}, where atoms can readily detach from Cu clusters, one anticipates a natural growth instability wherein the larger clusters in the population tend to grow much faster by incorporating atoms detaching from smaller clusters (a process also known as Ostwald ripening) [40–42]. The driving force is the lower chemical potential of the larger clusters, as quantified by the Gibbs–Thompson relation. In fact, smaller clusters at defects can potentially shrink and effectively disappear. This picture explains the existence of two populations of clusters in our system, where the larger sizes result from the growth instability. At 780 K, both populations are present in significant numbers. At 900 K, it appears that only the larger clusters survive, having consumed most of the smaller clusters.

4.3. Pyramidal growth shapes

Another issue is the mechanism that leads to pyramidal growth shapes. The data show that below 780 K, non- pyramidal irregular clusters dominate, and above 780 K, pyramidal clusters dominate, while the two forms coexist at 780 K. We propose that the pyramids require a more perfect atomic Cu fcc order at the interface with the MoS₂ substrate than the irregular clusters, and that the formation of a long-range (111) plane at this interface is an activated process, requiring higher temperature than the less-ordered interfaces that underlie the irregular clusters. We propose that whether a small cluster develops into a pyramid or another type of shape is contingent upon the activated formation of a base that has long-range epitaxy with the substrate, which begins at 780 K under our conditions.

Assuming a perfect interface, clusters might be expected to develop as six-sided pyramids, reflecting the six-fold symmetry of both the MoS₂ surface plane and individual Cu(111) layers. In the simplest scenario, the Cu pyramidal sides would alternate between (100) and (111) facets. Then, employing general concepts from Frank’s model of crystal growth [31], if one type of side facet grows faster than the other, that type will grow out and disappear, leaving a three-fold triangular pyramidal structure. This seems a plausible scenario for the development of pyramids in the Cu/MoS₂ system. However, this picture is incomplete, since the observed pyramid sides are neither (100) nor (111) facets. Instead, one can think of the (311) planes as being highly-stepped (111) surfaces that expose (100) microfacets, as shown in figure 8. The explanation for the (311) slope selection must involve details of Cu mass transport up and down sides of pyramids with various slopes and structures.

4.4. Comparisons with other systems

In general, 2D materials have much lower surface energies than metals, so the general expectation (assuming that low surface energies translate to low adhesion energies) is that metals will grow as 3D clusters (Volmer Weber growth) on these surfaces. Indeed, fundamental studies of metal growth show that this expectation is generally met for metals grown on graphene [43] and graphite [44] in vacuum. Fundamental studies of metal growth on transition metal dichalcogenides in vacuum are rarer, to date, but they indicate a more complex scenario. In a comparative study of three metals on MoS₂, Gong et al. [45] showed that Pd grows layer-by-layer followed by 3D clustering (Stranski–Krastanov growth), whereas Au and Ag simply grow as 3D clusters. Strong Pd–S covalent interactions may account for the initial wetting layer formed by Pd [46].

Some previous studies of metal growth on a 2D material have revealed the large, 3D, faceted types of metal clusters observed in this work. Au islands with triangular bases were observed on the (0001) surface of graphite, as well as pentagonal bipyramids [30]. Faceted crystallites of Pb on graphite have also been analyzed in detail [31, 47]. But the relatively limited number of such observations is probably because other fundamental studies have typically focused on room temperature deposition with lower fluxes. Our work is somewhat unusual in focusing on higher-temperature deposition where desorption is active (incomplete condensation), with relatively high flux and high exposures. The high flux and high exposures serve to build up metal coverage even in the face of active desorption.
5. Conclusions

When MoS$_2$ is exposed to Cu at 300 K, the density of Cu clusters is comparable to the density of defects on the clean MoS$_2$ surface. At higher deposition temperatures, and with long deposition times (high Cu exposures), Cu clusters are larger and less dense, and they often assume irregularly faceted or polyhedron-like shapes which are far different than the equilibrium shape. One particular type of polyhedron-like shape emerges at 780 K and predominates at 900 K: a pyramidal cluster with three (311) planes as side facets. This shape may require activated formation of a well-ordered coincidence lattice as its base. The condensation coefficient of Cu is small during deposition at elevated temperatures, but Cu clusters act as traps for self-condensation. The Cu retains its metallic character at all temperatures investigated; there is no reaction with the MoS$_2$ substrate. The island area distribution is bimodal, and in some cases large Cu clusters are surrounded by denuded zones. We propose that coarsening is operative during growth at elevated temperatures, as well as defect-mediated nucleation.

Acknowledgments

This work was supported primarily by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. Research was performed at the Ames Laboratory, which is operated by Iowa State University under contract # DE-AC02-07CH11358. The experimental work was performed or supervised by DJ, ALR, MCT, PAT,QL, and JK. Theoretical work was performed or supervised by KCL and JWE, and was supported by the U.S. DOE, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division. QL and JK were partially supported by the National Science Foundation through grant CMMI-1760348.

ORCID iDs

Dapeng Jing https://orcid.org/0000-0001-7600-7071
Ann Lii-Rosales https://orcid.org/0000-0002-8218-248X
King C Lai https://orcid.org/0000-0003-2764-356X
Qiang Li https://orcid.org/0000-0002-0701-8479
Jaeyoun Kim https://orcid.org/0000-0003-4449-317X
Michael C Tringides https://orcid.org/0000-0001-5003-7280
James W Evans https://orcid.org/0000-0002-5806-3720
Patricia A Thiel https://orcid.org/0000-0003-4195-0216

References

[1] Gupta T 2009 Copper Interconnect Technology (Berlin: Springer)
[2] Havemann R H and Hutchby J A 2001 High-performance interconnects: An integration overview Proc. IEEE 89 586–601
New J. Phys. 22 (2020) 053033

[3] Shen T T, Valencia D, Wang Q X, Wang K C, Povolotskyy M, Kim M J, Klimeck G, Chen Z H and Appenzeller J 2019 MoS$_2$ for enhanced electrical performance of ultrathin copper films ACS Appl. Mater. Interfaces 11 28345–51

[4] Li L, Chen X Y, Wang C H, Cao J, Lee S, Tang A, Ahn C, Roy S S, Arnold M S and Wong H S P 2015 Vertical and lateral copper transport through graphene layers ACS Nano 9 8361–7

[5] Mehta R, Cugh S and Chen Z 2017 Transfer-free multi-layer graphene as a diffusion barrier Nanoscale 9 1827–33

[6] Lo C L, Catalano M, Smith K K H, Wang I H, Zhang S J, Pop E, Kim M J and Chen Z H 2017 Studies of two-dimensional h-BN and MoS$_2$ for potential diffusion barrier application in copper interconnect technology npj 2D Mater. Appl. 1 42

[7] Xia B R, Guo Q, Gao D Q, Shi S P and Tao K 2016 High temperature ferromagnetism in Cu-doped MoS$_2$ nanosheets J. Phys. D 49 165003

[8] Yue Q, Chang S L, Qin S Q and Li J B 2013 Functionalization of monolayer MoS$_2$ by substitutional doping: a first-principles study Phys. Lett. A 377 1562–73

[9] Cheng Y C, Zhu Z Y, Mi W B, Guo Z B and Schwinghammer U 2013 Prediction of two-dimensional diluted magnetic semiconductors: Doped monolayer MoS$_2$ systems Phys. Rev. B 87 104401

[10] An V, Anisimov E, Druzyanova V, Burtsev N, Shakleva I and Khaskelberg M 2016 Study of tribological behavior of Cu-MoS$_2$ and Ag-MoS$_2$ nanocomposite lubricants SpringerPlus 5 72

[11] An V and Irtegov Y 2014 Tribological properties of nanolamellar MoS$_2$ doped with copper nanoparticles J. Mat. Sci. 49 731073

[12] Attanayake N H, Thenuwara A C, Patra A, Aulin Y V, Tran T M, Chakraborty H, Borguet E, Klein M L, Perdew J P and Strongin D R 2018 Effect of intercalated metals on the electrocatalytic activity of 1T-MoS$_2$ for the hydrogen evolution reaction ACS Energy Lett. 3 17–19

[13] Kim D, Sun D Z, Lu W H, Cheng Z H, Zhu Y M, Le D, Rahman T S and Bartels L 2011 Toward the growth of an aligned single-layer MoS$_2$ film Langmuir 27 11650–3

[14] Han Y, Tringides M C, Evans J W and Thiel P A 2020 Adsorption, intercalation, diffusion, and adhesion of Cu at the 2H-MoS$_2$ (0001) surface from first-principles calculations Phys. Rev. Res. 2 013182

[15] Burns R P, Pierce D E, Dauplaise H M, Gabriel K A and Mizerka L I 1998 Evaluation of solid lubricants: temperature programmed desorption of Mo$_2$S$_3$ on molybdenum and of ion-implanted Mo$_2$S$_3$ on molybdenum Defense Technical Information Center, U.S. Army Materials Technology Laboratory, Watertown, MA, ADA203741

[16] Donarelli M, Bisti F, Perrozzi F and Ottaviano L 2013 Tunable sulfur desorption in exfoliated MoS$_2$ by means of thermal annealing in ultra-high vacuum Chem. Phys. Lett. 588 199–202

[17] Addou R et al 2015 Impurities and electronic property variations of natural MoS$_2$ crystal surfaces ACS Nano 9 9124–33

[18] Silly F and Castell M R 2009 Temperature-dependent stability of supported five-fold twinned copper nanocrystals ACS Nano 3 901–6

[19] Yang H J, He S Y and Tuan H Y 2014 Self-seeded growth of five-fold twinned copper nanowires: mechanistic study, characterization and SERS applications Langmuir 30 602–11

[20] Han Y, Lai K C, Han Y, Spurgeon P, Huang W, Thiel P A, Liu D J and Evans J W 2019 Reshaping, intermixing, and coarsening for Fe nanocrystals encapsulated at the graphite surface Surf. Sci. 731 073

[21] Kern R and Müller P 2000 Equilibrium nano-shape changes induced by epitaxial stress (generalised Wulff-Kaishew theorem) Surf. Sci. 457 229–33

[22] Kaischew R 1953 Über eine verallgemeinerung des Wulffschen satzes und über die kristallbildung auf fremden oberflächen Arbeitsstatung Festkörper Phys. 1953 81–13

[23] Lii-Rosales A, Han Y, Julien S E, Pierre-Louis O, Jing D, Wang K T, Tringides M C, Evans J W and Thiel P A 2020 Shapes of Fe and Ni nanocrystals: Nonequilibrium statistical mechanical and coarse-grained modeling J. Appl. Phys. 131 55–60

[24] Winterbottom W L 1967 Equilibrium shape of a small particle in contact with a foreign substrate J. Vac. Sci. Technol. B 35 289–99

[25] Kern R, Le Lay G and Metois J J 1979 Basic mechanisms in the early stages of epitaxy Surf. Sci. 81–3 303–10

[26] Pimpinelli A and Villain J 1998 Physics of Crystal Growth (Cambridge: Cambridge University Press)

[27] Bansal B, Gokhale M R, Bhattacharya A and Arora B M 2007 InAs/InP quantum dots with bimodal size distribution: two independent mechanisms Surf. Sci. 554 50–63

[28] Miranda R and Gallego J M 2001 Bimodal island-size distributions in submonolayer growth Surf. Sci. 487 136–45

[29] Evans J W, Thiel P A and Bartelt M C 2006 Morphological evolution during epitaxial thin film growth: formation of 2D islands and 3D mounds Surf. Sci. Rep. 61 1

[30] Mulheran P A and Blackman J A 1995 The origins of island size in heterogeneous film growth Phil. Mag. Lett. 72 55–60

[31] Han Y, Gaudry E, Oliveira T J and Evans J W 2014 Self-seeded growth of five-fold twinned copper nanowires: mechanistic study, characterization and SERS applications Nanoscale 6 731073

[32] Kern R and Müller P 2000 Equilibrium nano-shape changes induced by epitaxial stress (generalised Wulff-Kaishew theorem) Surf. Sci. 457 229–33

[33] Kaischew R 1953 Über eine verallgemeinerung des Wulffschen satzes und über die kristallbildung auf fremden oberflächen Arbeitsstatung Festkörper Phys. 1953 81–13

[34] Lii-Rosales A, Han Y, Julien S E, Pierre-Louis O, Jing D, Wang K T, Tringides M C, Evans J W and Thiel P A 2020 Shapes of Fe and Ni nanocrystals: Nonequilibrium statistical mechanical and coarse-grained modeling J. Appl. Phys. 131 55–60

[35] Winterbottom W L 1967 Equilibrium shape of a small particle in contact with a foreign substrate J. Vac. Sci. Technol. B 35 289–99

[36] Pimpinelli A and Villain J 1998 Physics of Crystal Growth (Cambridge: Cambridge University Press)

[37] Bansal B, Gokhale M R, Bhattacharya A and Arora B M 2007 InAs/InP quantum dots with bimodal size distribution: two independent mechanisms Surf. Sci. 554 50–63

[38] Miranda R and Gallego J M 2001 Bimodal island-size distributions in submonolayer growth Surf. Sci. 487 136–45

[39] Evans J W, Thiel P A and Bartelt M C 2006 Morphological evolution during epitaxial thin film growth: formation of 2D islands and 3D mounds Surf. Sci. Rep. 61 1

[40] Mulheran P A and Blackman J A 1995 The origins of island size in heterogeneous film growth Phil. Mag. Lett. 72 55–60

[41] Han Y, Gaudry E, Oliveira T J and Evans J W 2014 Self-seeded growth of five-fold twinned copper nanowires: mechanistic study, characterization and SERS applications Nanoscale 6 731073
[45] Gong C et al 2013 Metal contacts on physical vapor deposited monolayer MoS ACS Nano 7 11350–7
[46] Wu P, Huang M, Yin N Q and Li P 2019 The modulation effect of MoS$_2$ monolayers on the nucleation and growth of Pd clusters: first-principles study Nanomaterials 9 395
[47] Heyraud J C and Metois J J 1982 Mechanisms of morphological change during the establishment of the equilibrium shape: lead on graphite J. Cryst. Growth 82 269–73