

Reaction pathways in the oxidation and pesting of molybdenum disilicide MoSi₂ studied with scanning tunneling microscopy and spectroscopy



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ABSTRACT

The oxidation and pesting of Molybdenum Disilicide is a critical limiter in its technical use. The materials disintegration during the pesting reaction in cracks and at grain boundaries prevents direct observation of the process. A model system consisting of silicide crystallites on a Si(001) surface was developed to study the progression of the oxidation reaction *in-situ* with Scanning Tunneling Microscopy and Spectroscopy. Deposition and annealing of Mo thin films is used to synthesize crystallites in a size range between 10 and 100 nm, and atomic resolution is achieved on several facets. The MoSi₂ is oxidized in the temperature range 400–800°C bracketing the pesting regime and beyond, combined with molecular oxygen exposure from 2 to 100 Langmuir. The oxidation process can be subdivided in three distinct regimes defined by their respective oxidation conditions: regime 1 (incubation) where only subtle changes in the electronic structure of the crystallites occurs, to regime 2 with a rapid increase in the crystallite density due to the volume gain of the pesting reaction transforming silicide to oxide, and regime 3 where a silica layer starts to form. The incubation time is attributed to oxygen dissolution and/or formation of a ternary Mo-Si-O phase, which is followed by the release of MoO_x molecules. The diffusion of MoO_x triggers secondary nucleation events, and contributes to the accelerated oxidation of the surface. Increasing the surface temperature > 650°C promotes desorption and sublimation over diffusion and supports silica formation. This study unraveled the intermediate reaction steps of silicide oxidation, and specifically underscores the critical role of reactant diffusion in the rapid progression of the pesting reaction.

1. Introduction

The Mo-Si alloy system has been intensely studied as a candidate for high temperature structural applications due to its superior oxidation resistance, high melting point, and high strength [1,2]. This system is comprised of three intermetallic phases, Mo₃Si (A15), Mo₅Si₃ (T1), and MoSi₂. The MoSi₂ phase exhibits excellent oxidation resistance from 1000–1250°C due to the formation of a protective silica scale [1,2]. A primary drawback of MoSi₂ is the oxidation reaction prior to silica formation where a process described as pesting occurs [3].

First defined by Fitzer in 1956, pesting is the disintegration of MoSi₂ into powder during thermal oxidation in the temperature range between 400 and 600°C [3]. A generally accepted explanation for the pesting mechanism includes the formation of Molybdenum and Silicon oxide species, which form preferentially at high surface energy locations, specifically, cracks and pores in the sample. The large volume expansion associated with the formation of the oxide species, specifically MoO₃, produces internal stresses resulting in the mechanical

disintegration of the sample [1,2]. Past approximately 600°C pesting is no longer observed and the formation of amorphous SiO₂ layers has been attributed to the increased volatility of MoO₃ as it approaches its melting temperature of 795°C. Thus, there is no longer a build-up of oxide species at the pores or cracks which produced the internal stress that caused pesting of the sample [1,2]. The interplay between mixed oxide formation in the pesting regime and the transition out of this regime due to the volatilization of MoO₃ are critical aspects that govern the oxidation of MoSi₂ prior to protective silica formation.

A variety of different experimental techniques have been used to study the pesting reaction, however, understanding the evolution of this process with high spatial resolution has yet to be achieved. This work aims to accomplish this feat by studying the oxidation of nanometer-scale MoSi₂ crystallites with the use of Scanning Tunneling Microscopy/Spectroscopy (STM/STS). This experimental approach provides the advantage of understanding the evolution of the pesting reaction down to the atomic scale by carrying out the oxidation on a surface. In addition, the nanometer-scale MoSi₂ crystallites have a high surface

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energy, mimicking pores or cracks in bulk MoSi₂ samples, which is the preferential region where Mo-oxide species nucleate eventually leading to pesting. This study will also focus on understanding the transition out of the pesting regime as the oxidation temperature exceeds 600°C and MoO₃ starts to volatilize from the surface. Thus, the objective of this work was to investigate the initial stages of oxidation for MoSi₂ in the temperature range of 400–800°C which brackets the pesting regime, with high spatial resolution.

2. Experimental

This study utilized STM/STS to probe the structural and electronic features associated with the formation and oxidation of MoSi₂ crystallites with high spatial resolution. The crystallite synthesis and oxidation experiments were performed *in-situ* in an ultra-high vacuum (UHV) preparation chamber with a base pressure of $< 3 \times 10^{-10}$ mbar, which is coupled to an Omicron Nanotechnology Variable Temperature Scanning Probe Microscope (VT-SPM). The *in-situ* preparation and oxidation of MoSi₂ enabled us to study this reaction process in a highly controlled manner.

Nanoscale MoSi₂ crystallites were prepared by depositing Molybdenum on a Si(001)–(2 × 1) substrate at (i) room temperature followed by an annealing step, or (ii) deposition of Mo on a hot substrate to trigger the formation of significantly larger crystallites owing to the enhanced diffusivity of the reactants. The deposition and oxidation conditions for all samples are summarized in Table 1. The Si (001) substrate was annealed overnight at 400°C followed by flash annealing using the procedure described in a publication by Hata et al., which leads to the (2 × 1) surface reconstruction with few defects [4]. Subsequently, 0.1–1.5 nm of Mo (American Elements, 99.95%) was deposited at a rate of 0.2 nm/min via electron beam evaporation with a MANTIS EV mini e-beam evaporator. The deposition rate was adjusted using an Inficon Quartz Crystal Monitor (QCM). During the subsequent annealing Mo and Si undergo a solid state reaction producing the MoSi₂ crystallites with the di-silicide phase forming preferentially due to the

Table 1

Synthesis and Oxidation: Summary of all processing conditions for synthesis of silicide, and subsequent oxidation. Imaging was performed after each oxidation step, e.g. Sample #2 was subjected to two consecutive oxidation steps at 550°C interrupted by imaging at room temperature. For Sample #1 to #6 Mo deposition was performed at room temperature with an additional annealing step to form silicide, and for samples #A to #D the Mo deposition was done on a hot substrate without additional annealing. For sample #3 two data points with 600°C (sample center) and 650°C (T) were recorded simultaneously exploiting a thermal gradient on the sample.

Sample Number	MoSi ₂ Synthesis Data in Fig. 1		Oxidation Parameters Data in Fig. 2
	Mo Coverage (ML)	Annealing Temperature (°C)	Exposure Amount (L)-Temperature (°C)
1	2.30	650	5 L + 6 L—all at 550°C 11 L Total
2	2.30	725	10 L at 750°C
3	1.95	600	7 + 8 + 15 L—all at 600°C 30 L Total
4	2.2	650 (T) 675	5 L at 600°C + 5 L at 650°C 10 L Total
5	2.75	650	13 L at 600°C
6	3.05	750	23 L at 600°C
A	1.1	575	2 L at 400°C
B	1.75	550	20 + 30 L—all at 725°C 50 L Total
C	1.25	550	25 + 75 L—all at 675°C 100 L Total
D	1.25	550	100 L at 800°C

large Si reservoir coming from the underlying Si substrate [5–8]. The MoSi₂ crystallites were oxidized by introducing 99.997% dry O₂ into the preparation chamber. The oxygen exposure amounts and annealing temperatures are provided in Table 1. Our oxidation parameter space ranged from 2 to 100 L with annealing temperatures from 400 to 800°C. In this work, we maintained the same $p(\text{O}_2) = 1.3 \times 10^{-8}$ mbar for all oxidation experiments.

Topography images and ST spectra were recorded prior to oxidation, and after each individual oxidation step. Images were recorded at various locations on the sample to probe the homogeneity of the silicide crystallite distribution. Typical imaging conditions used for the topographic scans are a bias voltage of $V_B = -2.0$ V, and a tunneling current of $I_t = 0.1$ nA unless otherwise noted. The STM images were analyzed with WSxM, an open source software package [9]. The electronic signature and local density of states (LDOS) were analyzed by collecting STS maps, which are produced by acquiring current-voltage (I-V) characteristics at regularly spaced locations (every third pixel of the topography image) on the sample within an image. The tip is held at a fixed position above the surface, and voltage sweep is applied to the tip while recording the tunneling current with an open feedback loop. The simultaneous acquisition of spectroscopy and topography data allows for correlation between surface features and electronic signature, and facilitates averaging to improve the signal to noise ratio. Following the procedure described by Feenstra et al., the I-V curves are differentiated and normalized producing the expression, $(dI/dV)/(I/V + \epsilon)$, which is proportional to the local density of states (LDOS) of the sample at the surface [10]. The additional (small) ϵ term is used to avoid division by zero around the Fermi energy and it is chosen accordingly to make sure that the spectra are not distorted. A MATLAB code was used to assemble STS maps to facilitate correlation between topography features and electronic information, and selectively extract ST spectra from specific locations [11]. A typical voltage sweep is $V_B = -2$ to 2 V with $\Delta V = 0.04$ V.

The assessment of the band gap, which is one of the most prominent features in STS, is not an unambiguous method to determine the chemical nature and composition of ultrathin films and surfaces [10]. For example, ultrathin (insulating) layers and crystallites will express a smaller gap than the corresponding bulk material due to confinement, and interaction with a metallic or semiconducting substrate. The same holds true for highly defective, or amorphous materials. The arguments we make throughout this manuscript with respect to the crystallites/surface electronic structure are therefore interpreted nearly exclusively with respect to relative changes as the oxidation reaction progresses. The following qualitative arguments can be made about the expected modulation of the band gaps in our materials system:

- (1) The silicides MoSi₂ and Mo₅Si₃ have an extremely small gap, and are effectively metallic [12]. (2) All oxides such as MoO₃ and SiO₂ have larger bulk band gaps of -3.0 eV and 8.9 eV, respectively, due to the larger ionicity of the bond [13,14].
- (2) The band structure and gaps of ternary Mo-Si-O compounds will possess somewhat intermediate electronic signatures, with an increasing gap towards the oxygen-rich phases.

3. Results

The STM images in Fig. 1 illustrate the progression of the solid state reaction leading to the formation of MoSi₂. The deposition and oxidation conditions are listed for all samples in Table 1. Fig. 1A shows the pristine Si(001) substrate with the (2 × 1) dimer row surface reconstruction, and Fig. 1B displays a clustered Mo layer prior to annealing. Subsequent annealing drives the formation of MoSi₂ crystallites (sample #3), which is displayed Fig. 1C. The deposition on a hot substrate leads to the formation of significantly larger crystallites as shown in Fig. 1D and E (sample #A, $T = 575^\circ\text{C}$). The crystallites burrow deeply into the Si-surface since the reaction is controlled by

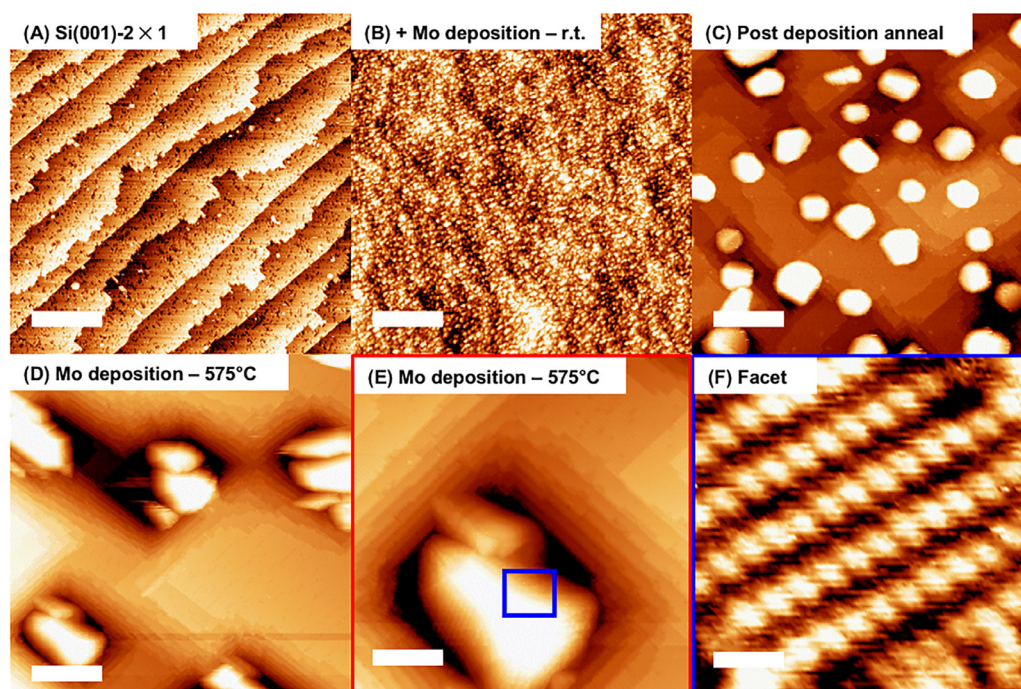
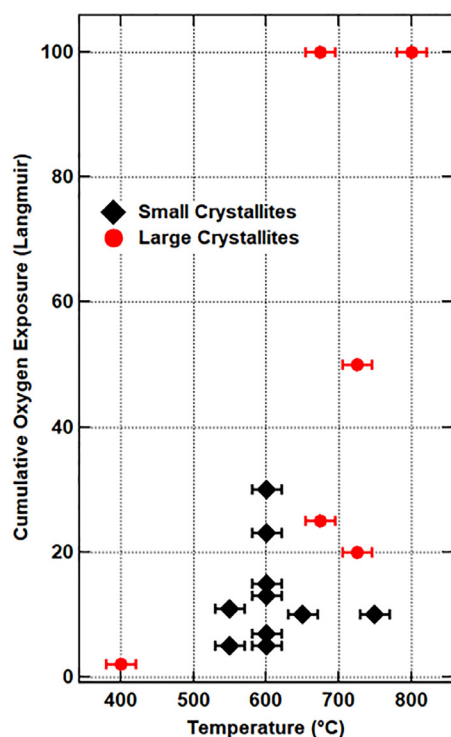


Fig. 1. Representative images to illustrate synthesis of MoSi_2 . (A) is the pristine $\text{Si}(001)-2\times 1$ reconstruction, (B) Mo-layer deposited at room temperature, (C) is after annealing of the Mo-layer to 600°C , which initiates the solid state reaction to form MoSi_2 (sample #3), and (D) large MoSi_2 crystallites obtained after deposition of Mo at 575°C (sample #A), and (F) shows an atomic resolution image of one of the facets from (E) Images (A)–(D) scale bar is 30 nm (image size $150\times 150\text{ nm}^2$), (E) scale bar-16 nm (image size $65\times 65\text{ nm}^2$), (F) scale bar-1 nm (image size $5\times 5\text{ nm}^2$).

highly mobile Mo-adatoms which react with the Si-substrate. Annealing during deposition promotes surface diffusivity and leads to the formation of larger crystallites and consequently a smaller crystallite density. The STM image in Fig. 1F reveals an atomically resolved facet, which has a striking similarity to the Si(001) dimer rows. Quite a few of the facets could be imaged with atomic resolution, and MoSi_2 synthesis at $T > 650^\circ\text{C}$ lead to the formation of silicene-terminated h- $\text{MoSi}_2(0001)$, which was reported recently [15].

The oxidation parameter space is visualized for all MoSi_2 samples in Fig. 2A and spans temperatures from 400 to 800°C , and oxygen exposures from 2 to 100 L. The outcome of the oxidation experiments specifically for small crystallites is summarized in Fig. 2B and three different regimes are distinguished: regime 1—minor changes in surface morphology and electronic structure, regime 2—rapid increase in crystallite density which can be described as “explosive multiplication”, and regime 3—oxide scale formation recognized by significant increase in

(A) Oxidation Parameter Space



(B) Oxidation Regimes for Small Crystallites

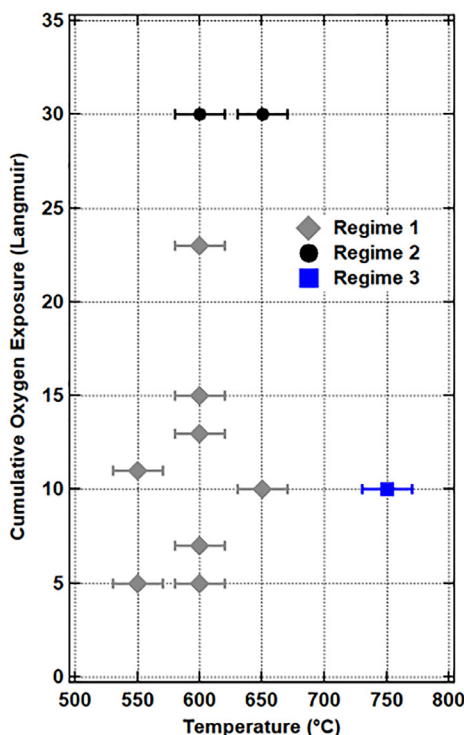


Fig. 2. (A) Summary of oxidation parameter space for all oxidation experiments including small crystallite samples (#1 to #6) and large crystallite samples obtained by Mo-deposition on a hot sample (#A to #D). (B) Oxidation regimes as defined for small crystallite samples only. The results are grouped into three regimes—regime 1: no morphological changes, regime 2: dramatic increase in the density of crystallites, and regime 3: formation of an oxide layer. Sample #3 discussed in Fig. 5 provided additional data on the transition between regime 1 and 2.

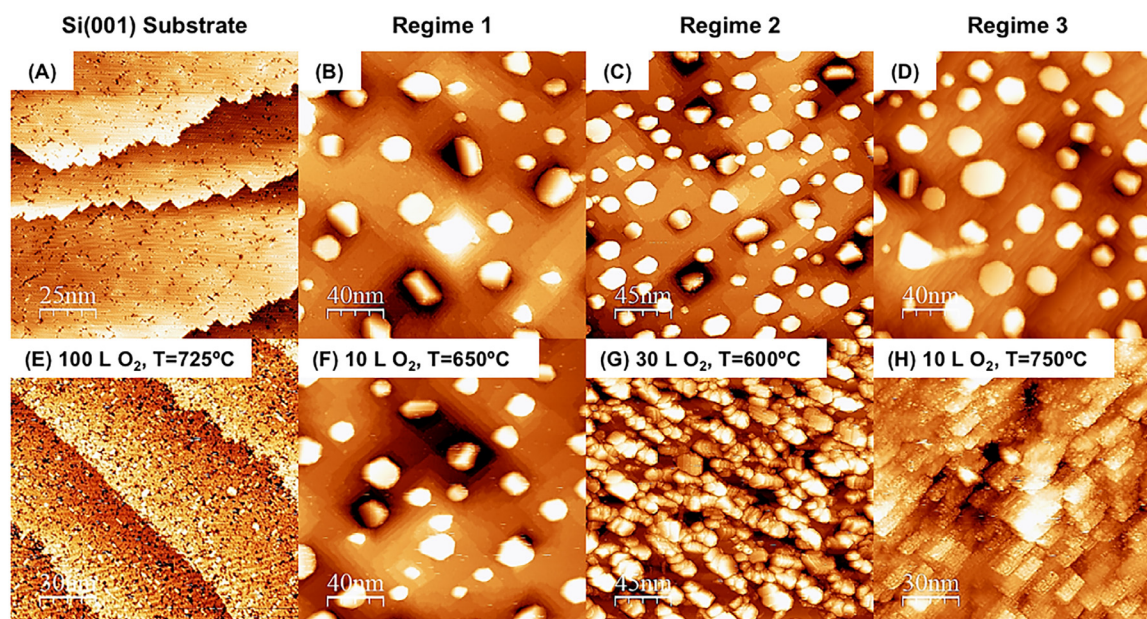


Fig. 3. Comparison of the individual oxidation steps. (A) and (E) show the reaction of the Si(001) – 2×1 substrate to oxidation. The oxidation conditions are harsher than any of the oxidation steps used in the silicide experiments. (B) and (F) correspond to regime 1 oxidation with subtle changes in electronic structure [sample #4], (C) and (G) reflect the rapid multiplication of crystallites on the surface in regime 2 [sample #3], and (D) and (H) show an example for regime 3 where the oxide layer formation is evident [sample #2].

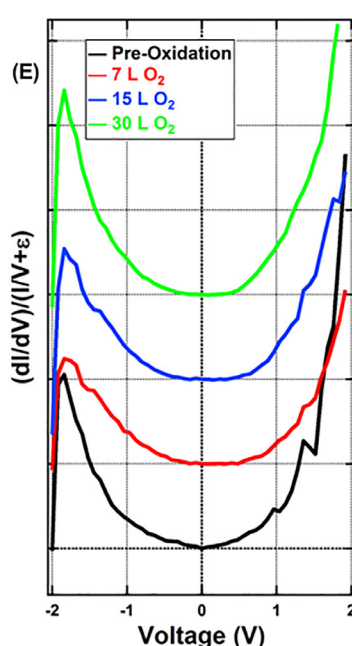
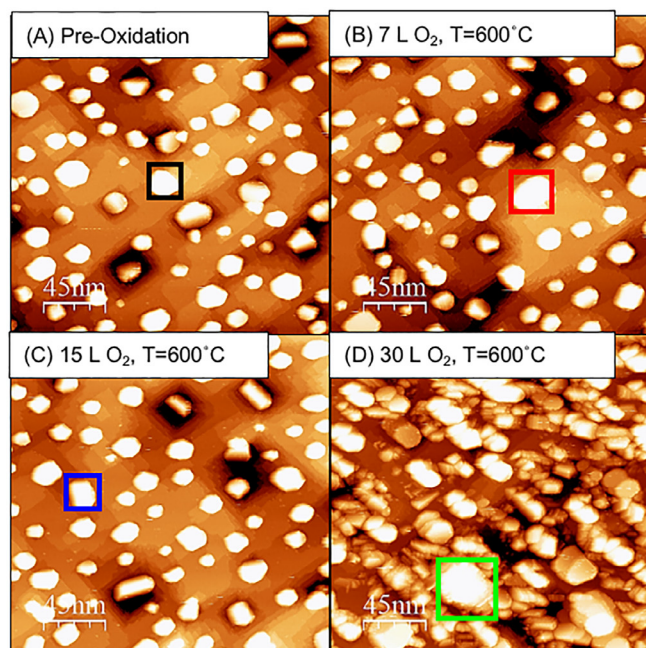


Fig. 4. Scanning tunneling microscopy topography images and spectroscopy showing the progression of oxidation for sample #4 from the silicide synthesis to the first (B) and second (C) oxidation step. The third oxidation step (D) corresponds to regime 2. (E) Summarizes the spectroscopy data for select crystallites marked in the images. The spectroscopy data are averaged over 5–30 individual spectra. Additional spectroscopy data are included in the Supplemental Information.

the surface band gap and characteristic changes in the surface morphology. Representative STM images from each regime are summarized in Fig. 3 with a direct comparison between “before” and “after” oxidation. The spatially resolved information on the electronic signature for all regimes is included in Fig. 4 through Fig. 7, and in the Supplemental Information S1. We will first address the results for the oxidation of small MoSi₂ crystallites in samples #1 to #6; the oxidation of larger crystallites #A to #D follows the same general trend but they develop more pronounced morphological inhomogeneities and are discussed separately towards the end of the results section.

Fig. 3.A shows the Si-substrate prior to Mo deposition, and after the surface was exposed to 100 L of O₂ at 725°C, which reaches far into the silicon oxide formation regime for silicide. The STM image in Fig. 3.E

was recorded after oxidation and displays an increase in the number of defects and a few ultra-small oxide particles but no extended oxide layer, which is consistent with prior oxidation studies performed on Si (001) surfaces [16–18]. The Si substrate, which is also visible in between the silicide crystallites for most oxidation experiments, retains its (2×1) reconstruction. Therefore, we can attribute the morphological and electronic changes initiated by oxidation directly to the presence of MoSi₂.

Fig. 3B and F illustrate the oxidation of sample #4, which is representative of regime 1 with no morphological changes upon oxygen exposure. Sample #3 shown in Fig. 3C and G illustrates the dramatic increase in crystallite density on the surface, which is reminiscent of volume expansion due to rapid oxide growth during the pesting

reaction and corresponds to regime 2. A layer with a distinct scale-like morphology (Fig. 3H) dominates the surface at elevated temperatures in regime 3 and is tentatively attributed to SiO_2 or SiO_x .

Fig. 4 summarizes the transition from regime 1 to 2 and shows MoSi_2 crystallites that were subjected to 7, 15, and 30 L of O_2 at 600°C . No morphological changes are observed for the first two oxygen exposures (Fig. 4B and C) and the last image in Fig. 4D reveals the explosive increase in crystallite density after 30 L exposure. The crystallites densely populate the surface and only small sections of $\text{Si}(001)$ remain exposed. This is notably different from the more common oxidation reactions for alloy surfaces, where nucleation and growth progresses much more gradually [19,20]. ST spectra for each step of the reaction sequence are extracted and the corresponding crystallite is marked in the STM images with color-coded boxes and displayed in Fig. 4E. Each spectrum is averaged over several spectra collected on the respective crystallite.

The MoSi_2 crystallites display a nearly metallic signature prior to oxidation with a band gap of $< 0.2\text{ eV}$ [10]. After being exposed to oxygen, the band gaps increase and values between 0.3 and 0.8 eV, which excludes the formation of metallic Mo_5Si_3 and points to the formation of different oxide phases such as MoO_x , SiO_x and maybe even a ternary Mo-Si-O phase [21]. The transient formation of ternary compounds Mo-Si-O has already been suggested by Chou et al. as an intermediate reaction step at moderate temperatures, and can account for the modulation in electronic signatures [22,23]. The changes in the electronic signature show that the silicide is modified even before morphological changes are observed, and a complex set of intermediate and/or defect-rich crystallites is still present after 30 L exposure. A larger STS dataset for sample #3 after 30 L exposure is included in the Supplemental Information S1 and illustrates the variability in LDOS between crystallites extending from 0.2 to 2 eV indicating different reaction rates. The crystallite corners, and facets are mostly retained throughout the oxidation process, and atomic resolution images do not show oxygen as a surface adsorbate, which suggests a reaction pathway via the substrate-silicide interface or the crystallite bulk. The solubility of oxygen in MoSi_2 is very low at these temperatures, although a defect-assisted diffusion mechanisms could nonetheless contribute to O-enrichment of the bulk [1] and subsequent transformation to a mixed phase.

Fig. 5 illustrates in more detail the very narrow temperature range where the transformation from single isolated crystallites (regime 1) to rapid multiplication of crystallites (regime 2) occurs, along with a cartoon illustrating the temperature gradient on the Si substrate. We

take care to compare the progression of reactions and oxidation steps for regions on the Si-substrate with the same temperature—usually the center and right hand side of the sample, which accounts for 70% of the total sample area. Due to the use of direct current heating the left side of the sample, close to the clamp, will be hotter than the sample center which gave us the opportunity to observe the transition between regime 1 and 2 on a sample exposed to otherwise identical oxidation cycles. In the case of sample #3 the temperature range covered between sample center and the “hot” side of the sample traverses the boundary for crystallite reaction onset. Fig. 5A, recorded on the “hot” side of the sample at 650°C , is equivalent in exposure to sample Fig. 4B (600°C). Secondary nuclei have formed and are positioned close to the original crystallites. The higher temperature accelerates the oxidation reaction, which starts in the vicinity of the MoSi_2 crystallites and is initiated by short range diffusion of MoO_3 or other volatile Mo-oxidation products, and their reaction with the Si-substrate [24,25]. At larger oxygen exposure this process continues until the whole surface is covered with a dense population of crystallites.

The oxidation of sample #2 at 750°C (Fig. 6) leads to the formation of a continuous surface layer, which is structurally and electronically distinct compared to the oxide islands in regime 2. The layer appears crystalline and spans hundreds of nanometers on the surface interspersed with a few partially reacted crystallites (Fig. 6B). The morphology of the thin oxide layer is defined by rectangular strips separated by small grooves, which follow the terrace structure defined by the underlying $\text{Si}(001)$ substrate and the band gap of this layer is approximately 1.75 eV (Fig. 6C). Fig. 6C also includes an ST spectrum from a MoSi_2 crystallite embedded in the oxide layer, which has not yet completed the reaction with oxygen, and presents a smaller band gap. The surface layer with its rectangular strips is interpreted as a defective and ultrathin layer of SiO_x .

The oxidation of the large MoSi_2 crystallites leads to highly complex surfaces comprised of many heterogeneous structures, with an example being shown in Fig. 7- sample #C. Sample #A was only exposed to 2 L of oxygen at 400°C and retained its morphology-images after oxidation are indistinguishable from pre-oxidation crystallites shown in Fig. 1. Samples #B and #D were oxidized at $T > 700^\circ\text{C}$ and exhibit extremely heterogeneous surface morphologies, with select regions containing structures reminiscent of the rectangular oxide layer from regime 3 (Fig. 6). Examples of these surfaces are included in the Supplemental Information S2. The large crystallites are between 40 and 70 nm in diameter and are usually separated by a distance exceeding 100 nm. In comparison, the small crystallites in samples #1 to #6 are at most half

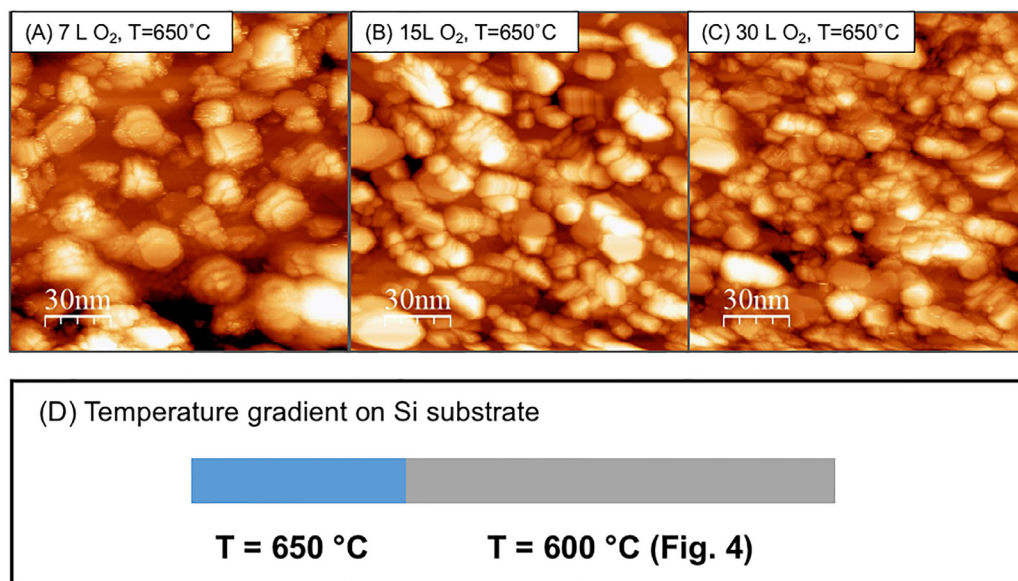


Fig. 5. (A)–(C) Scanning tunneling microscopy images showing the progression of oxidation for sample #3. The images are recorded on the section of sample #3, which is at 650°C as schematically shown in (D). (D) Cartoon illustrates the thermal gradient on the Si substrate due to the direct current heating geometry. The oxidation steps are identical to those shown in Fig. 4 for oxidation at 600°C for sample #3.

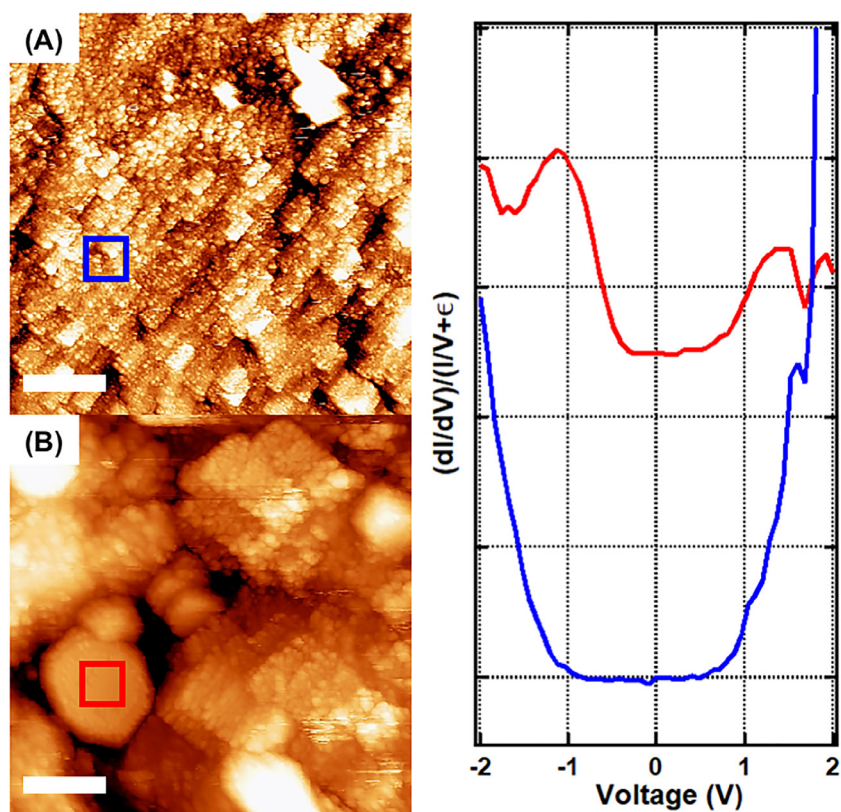


Fig. 6. Images and spectra for sample #2—the spectra are averaged over the areas marked in the images. (A) and (B) are positioned in regime 3. The ST spectra included in (C) illustrate the significant changes in electronic structure. The spectrum, which corresponds to image (B) was recorded on a h-MoSi₂ crystallites with a silicene termination. (A) Scale bar—40 nm. (B) Scale bar—16 nm.

this size and spaced only a few ten nanometers apart.

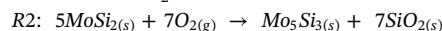
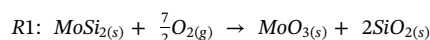
The large silicide crystallites reside in deep trenches on the surface as they burrow into the Si substrate due to the enhanced diffusivity of the adatoms. This local geometry is comparable to pores or cracks in bulk silicide samples. Fig. 7B. shows that the oxidation leads to a complete filling of the trenches and the formation of sizeable mounds on the relatively smooth Si surface. The mounds do not exhibit the characteristic sharp edges and well-defined facets previously observed for the silicide crystallites, and have a roughly bi-modal size distribution: large mounds with diameters of 80 nm or more, and smaller ones with diameters of less than 50 nm. The band gap for both mounds are approximately 1.0 eV (Fig. 7C). The behavior of sample #C during oxidation is commensurate with regime 2 reactions as defined for the smaller crystallites.

4. Discussion

The silicide crystallites, which are synthesized by a solid state reaction between Si(001) and Mo, provide a controlled template to study the oxidation reaction for MoSi₂. The majority of oxidation studies use zone refined polycrystalline materials, HIP (hot isostatic press) processed materials at different temperatures, or, in rare occasions, single crystals [1,26–28]. These materials are variable with respect to grain boundaries, cracks, and porosity and hence the results of oxidation experiments can differ widely obscuring the details of atomic scale reaction pathways. The use of surface crystallites mitigates many of the ambiguities encountered in the use of bulk materials, and enables us to focus on the chemical aspects of the oxidation as we cross the temperature range where pesting is typically observed. The large crystallites, which form in the high temperature deposition of Mo, mimic more closely the crack geometry since they are surrounded by deep grooves and burrow into the Si-surface. The Si(001) surface in between the crystallites is nearly inert to direct oxidation with O₂ within the MoSi₂ oxidation parameter space summarized in Fig. 2, but tends to react rapidly in the presence of volatile oxidation products from silicide

oxidation.

The oxidation of Mo-silicides is conventionally framed by oxidation regimes defined by temperature and described in detail by Berztiss et al. [1]. Pesting occurs in the temperature range of 400–600°C and is driven by the volume gain associated with the oxide products in chemical reactions R1 and R2. Either reaction pathway is feasible as both are calculated to have a negative Gibbs free energies [23].



Intermediate reaction steps including formation of ternary phases, and lower and non-stoichiometric oxides for Si and Mo are likely but currently not well understood. The signature of a “pesting reaction” is often used in the context of a chemical transformation in combination with the mechanical response due to the rapid volume gain in reactions R1 and R2. The mechanical response cannot be studied with surface crystallites but the volume gain in the chemical reactions, which trigger the mechanical response of pesting, are clearly seen in our experiments. The boundaries for the onset of pesting regime are seen for oxygen exposure of < 30 L and a temperature of about 650°C—the temperature limit is lower for high oxygen exposures as summarized in Fig. 2. Higher oxidizing temperatures will lead to the transition from a non-protective to a protective scale driven by increased volatility of the Mo-oxides and consolidation of the silica scale [1].

The regime 1 positioned at $T < 650^\circ\text{C}$ and exposure < 23 L is characterized by small changes in electronic structure expressed in the ST spectra in the absence of variations in morphology. We propose the electronic structure is modified by the introduction of oxygen in the silicide, and consequently formation of a ternary compound Mo-Si-O. The uptake of oxygen might be limited to the surface layers, or achieved by vacancy-assisted diffusion of oxygen into the crystallite bulk, which can overcome the low solubility of oxygen at this temperature. The limited literature on MoSi₂ thin film growth hints at the presence of sub-stoichiometric MoSi_{1.7}, which could facilitate oxygen transport

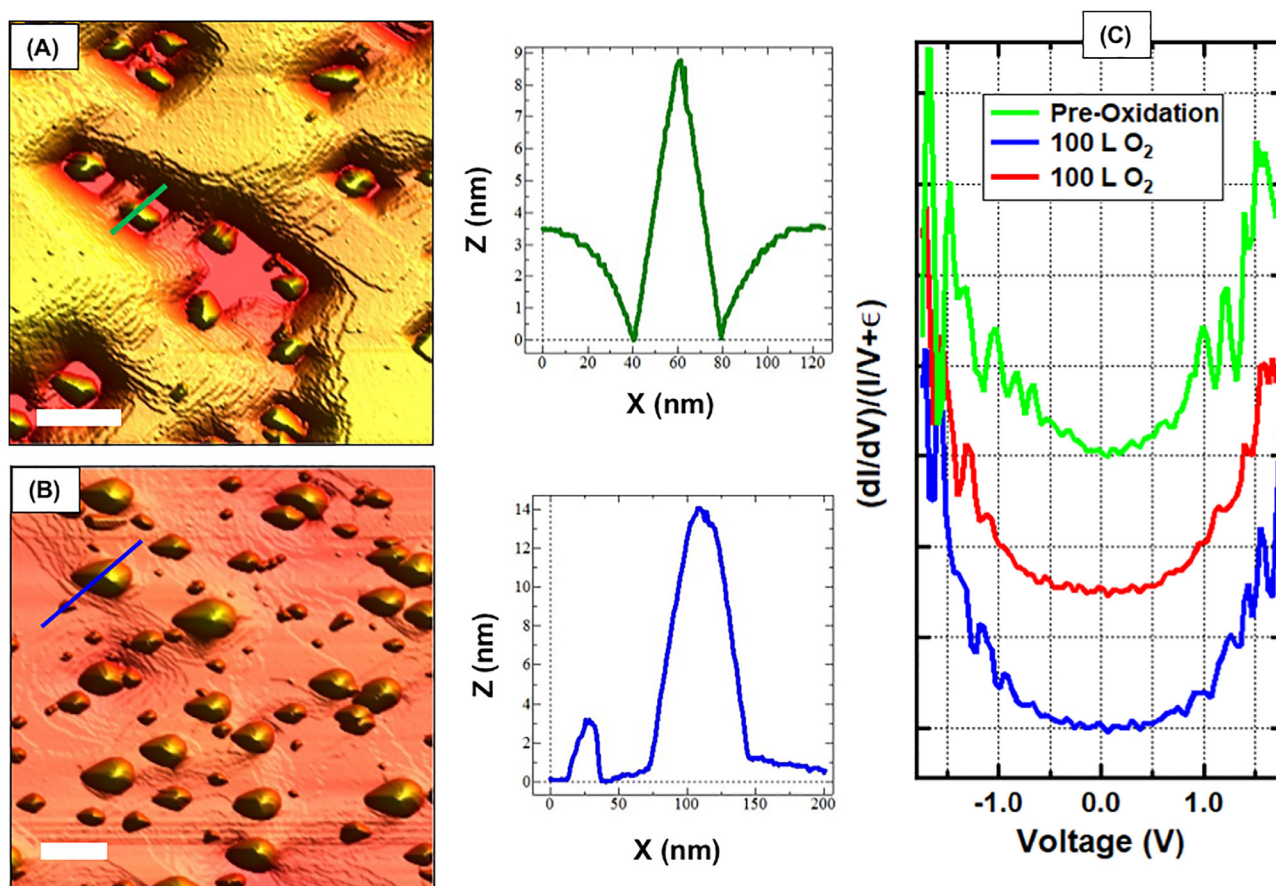


Fig. 7. (A) Sample #C before oxidation, image size $500 \times 500 \text{ nm}^2$ (scale bar–100 nm); (b) sample #C after oxidation, image size $650 \times 650 \text{ nm}^2$ (scale bar–100 nm); Selected linescans in the center panel show the large silicide crystallites burrowed into the Si-surface, and mounds observed after oxidation. (C) Spectra for MoSi₂ crystallites (pre-oxidation), and mounds after oxidation 100 L O₂.

[5,8]. The presence of defects at grain boundaries or non-stoichiometric surface layers will play a similar role in polycrystalline MoSi₂, and facilitate the uptake of oxygen and local transformation to ternary phases.

Regime 1 can be understood as an incubation period prior to the rapid multiplication of crystallites in regime 2. This observation is consistent with work performed by Chou et al. who studied the reaction kinetics of pesting for MoSi₂, and observed the reaction proceeded in a two-stage process [22]. We propose the following model: at a critical limit of Mo-Si-O composition the crystallites “break” and reactive Mo-oxide-molecules leach out. The oxide-molecules can desorb into the gas phase, diffuse along the surface, and re-adsorb on the surface. The temperature is still relatively low and it is expected that a significant percentage of oxide-molecules diffuse along the surface and desorption is limited. The Mo-oxides, which can include MoO₃ as well as MoO₂ diffuse along the surface and react with the underlying Si substrate to form additional crystallites. The transition from isolated crystallites to a high-density crystallite population is captured particularly well in Figs. 5 and 6. The Si-surface functions as a “detector” of surface oxide molecules. This enables us to distinguish between primary oxidation sites, and secondary oxidation sites which are formed due to reaction with surface oxides ejected during the primary oxidation reaction. The entirety of these reactions defines the “pesting chemistry”. The surface transport is recognized as a critical part of silicide oxidation, and surface diffusion of MoO_x at crack surfaces in bulk silicide, can account for the rapid formation of oxide particles.

This process is reminiscent of thermal or reactive spreading of MoO₃ which has been reported for MoO₃ catalyst particles on Al₂O₃, or SiO₂ oxide supports [23,24,28,29]. Rapid diffusion of MoO₃ molecules is driven by a concentration gradient on the surface, and a similar process

plays out in the silicide oxidation. However, in contrast to thermal spreading, Mo-oxide molecule diffusion leads to a secondary nucleation of Mo-(Si)-O crystallites with variable compositions. Si is likely incorporated via reactions with the Si-surface. Fig. 5 shows the onset of regime 2 particularly well—the secondary nucleation occurs close to and on the primary silicide crystallites and seems to favor high surface energy locations such as the edges. Continued oxygen exposure accelerates the reaction and as a result the entire surface is covered with a high density of crystallites. This reaction step reflects the progression of pesting chemistry. Surface transport of oxide-molecules and secondary nucleation events drive the reaction.

Regime 3 is positioned at the very boundary of our processing space (Fig. 2) and located at higher temperatures. It is characterized by a dramatically different, rectangular surface morphology, (near) complete coverage of the Si-surface, and a larger band gap. The temperature is above the pesting regime limits, and we therefore conclude that the oxide layer seen in Fig. 6 is dominated by a defective, and possibly sub-stoichiometric SiO_x. The samples exhibiting the rectangular oxide structure were oxidized at or above 700°C, which is a temperature range where MoO₃ becomes volatile - desorption now dominates over diffusive surface processes. This claim is supported by the scarcity of MoSi₂ crystallites as shown by Fig. 6. Si-oxide layers formed at the edge of the pesting regime after the complete loss of Mo-oxides are usually not yet protective and include numerous defects, which is commensurate with our observations [1,2]. Regime 3 oxide formation is governed by the sublimation of MoO₃ and thus exhibits a different oxidation mechanism compared to regime 2.

The control experiment performed with a bare Si(001) substrate without MoSi₂ crystallites was likewise positioned at the edge of the

peste regime temperature. Fig. 3A and E show the impact of 100 L of O₂ exposure at 725°C, and indeed only small oxide particles are seen despite the large oxygen exposure. This experiment further supports our model as described in the previous paragraphs, and underscores the critical role MoO₃ diffusion and sublimation play in the oxidation process. Clearly the secondary oxide crystallites seen in regime 2, and the oxide layer in regime 3 do not stem from the direct oxidation of Si (001) but are triggered by presence of silicide crystallites.

At last we can fully capture the observations made in the oxidation of large MoSi₂ crystallites which is summarized in Fig. 7 within the model developed in the previous paragraphs. The large crystallites are positioned at the bottom of trenches, which are bounded by sidewalls with a high concentration of highly reactive, under-coordinated Si step edges. Once the oxidation process moves into regime 2, and Mo-oxide molecules diffuse across the surface they will react with the step edges, and can prompt secondary nucleation events. However, secondary nucleation alone cannot explain the complete filling of the trenches and formation of a smooth Si(001) surface layer, but requires a high Si-atom surface mobility, or step-flow. We propose that a modulation of step edge energies, the Ehrlich–Schwöbel barrier, or Si-adatom mobility is caused by Mo-oxide adsorbates. This leads to the filling of trenches around the silicide crystallites. The trenches around the small crystallites are much less pronounced after synthesis, and the high crystallite density in regime 2 masks any trench-filling reaction. The very large mounds which emerge on the surface for sample #C are commensurate with the formation of secondary crystallites formed in this temperature regime. The overlapping diffusion fields and consequently supersaturation in Mo-oxide molecules in the small crystallite samples leads to a very dense population for small crystallites; for the large crystallites the density of secondary crystallites, respectively mounds, is, as expected, significantly lower. Oxidation of large crystallites at higher temperatures, which is shown in the supplemental information S2, leads to complex, highly corrugated oxide surface layers. The oxidation of large and small crystallites follows the same fundamental reaction pathways, which are controlled by Mo-oxide molecule diffusion, reaction, and sublimation.

5. Conclusions

The oxidation of MoSi₂ was studied using a model system of crystallites positioned on a Si(001) surface, which allows to monitor details of the reaction not otherwise accessible in bulk samples. The pristine Si-substrate is inert and does not oxidize within the oxidation parameter space used for silicide oxidation experiments. The initial stages of oxidation are characterized by an incubation period where subtle changes in electronic structure point to oxygen incorporation in the crystallite bulk or formation of ternary alloys. This is distinctly different from metal oxidation, which progresses by nucleation and growth of oxide islands. The transition to pesting is likely triggered by surpassing a critical limit in oxygen uptake defined by temperature and oxygen exposure which is followed by liberation of Mo-oxide molecules from the crystallites. The Mo-oxide molecules trigger the nucleation of secondary silicide and/or oxide crystallites following the reaction paths characteristic for pesting. However, Si(001) likely reacts with the Mo-oxide adsorbates and contributes to the secondary crystallite nucleation serving as a “detector” for the presence of reactive adsorbate. The presence of highly reactive Mo-oxide molecules will also contribute to the rapid progression of pesting reactions at silicide surfaces in cracks and at grain boundaries. A critical temperature has to be reached where Mo-oxide desorption is promoted over Mo-oxide surface diffusion to drive the formation of the desired silica scale. The role of surface diffusion of reactive oxides is critical to understanding, and in the future, control of the pesting reaction.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.susc.2018.11.015](https://doi.org/10.1016/j.susc.2018.11.015).

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