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Morphology and atomic structure of the sputtered and annealed Mo_3Si and Cr_3Si (110) surfaces

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Scanning tunneling microscopy was used to study the sputtered and annealed (110) surfaces of Mo_3Si and Cr_3Si. Both surfaces show extended and atomically flat terraces, but in the case of Mo_3Si there is also a uniform distribution of Mo crystallites. This difference in morphology is discussed in terms of different preferential sputtering effects. In both cases, measured step heights show that the ideally bulk-truncated surfaces are either purely Si or metal terminated. Atomically resolved images suggest that the Mo_3Si surface is Si terminated, but although no atomic resolution could be obtained for the Cr_3Si surface, there are indications that this surface is instead metal terminated.

The transition-metal silicides have been extensively studied in the past decades, mainly due to their applications in Si integrated-circuit technology.[1,2] These studies are directed to both the physical properties of the silicides as well as the compound formation itself, and large efforts have been made to understand the different metallurgical phases of these systems. In two recent papers, the low-index surfaces of bulk Mo_3Si and Cr_3Si crystals were examined by high-resolution photoelectron core-level spectroscopy.[3,4] In all cases, large surface Si 2*p* core-level shifts were observed, whereas no surface shifts could be deduced for the Mo 4*p* or Cr 3*p* components. From this, and the observation that the Si 2*p* component was affected much more rapidly upon oxygen or hydrogen adsorption, it was assumed that all these surfaces are Si terminated. These compounds solidify in the cubic A15 structure,[5] where the ideally bulk-terminated (110) surface top layer consists purely of either Si or metal atoms. A Si termination would also be in agreement with an apparent general tendency for transition-metal disilicides.[6]

In the present paper we used scanning tunneling microscopy (STM) to study the (110) surfaces of Mo_3Si and Cr_3Si prepared by sputtering and annealing in the same way as in the photoelectron spectroscopy studies. Both surfaces show extended flat terraces separated by step heights corresponding to a Si-Si bilayer or multiples thereof, but in the case of Mo_3Si there is also a high and uniform distribution of crystallite like islands. From the shapes and conductivity of these islands it is concluded that they consist of pure Mo. This difference is related to the sputtering-annealing process, where different preferential sputtering effects for the two silicides can be predicted. Atomically resolved images of the flat areas between the Mo islands indicate that these are bulk terminated with a topmost Si layer. The images of the Cr_3Si surface have a completely different character. No atomic resolution could be obtained in this case, but it is suggested that this surface instead might be metal terminated.

The experiments per performed in a UHV system with a base pressure better than 1×10^{-10} Torr. The growth and preparation of the Mo_3Si and Cr_3Si single crystals with mirror polished (110) surfaces are described elsewhere.[3,4] The samples were cleaned *in situ* by repeated cycles of 1-keV Ar^+ ion sputtering and annealings at different temperatures between 400 and 1000 °C. This produced well-defined (1×1) low-energy electron-diffraction patterns for both surfaces, although the diffraction pattern was sharper with a lower background for the Cr_3Si surface indicating larger terraces in that case. As will be shown, this observation is in good agreement with the STM results. The STM images were obtained with a commercial instrument (Omicron Vakuumphysik G.m.b.H.) using electrochemically etched tungsten tips.

Figures 1 and 2 show typical overview images of the two surfaces. The noisy character of the image in Fig. 1 is typical of the Cr_3Si surface, and strongly contrasts the

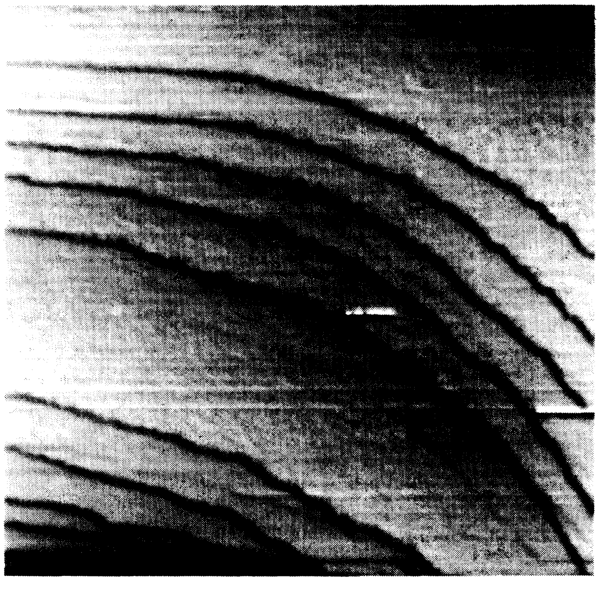

FIG. 1. A large-scale (2000×2000 Å^2) overview image of the Cr_3Si surface. The tunneling bias was 0.4 V and the current setting 1.0 nA.

stable tunneling conditions on the Mo_3Si surface. This unexpected finding will be further discussed below as a possible indication that these surfaces have quite different terminations. While the Cr_3Si surface was easily prepared to only expose extended flat terraces, the Mo_3Si surface always showed a high coverage of three-dimensional islands, typically 50 Å in height. As can be seen in Fig. 2, these islands have a crystalline character with well-defined facets often showing monatomiclike steps. The image is distorted due to influence from the tip structure,[7] but a careful inspection reveals that the islands in many cases show features corresponding well to bcc Mo. This pertains to the measured step heights, the overall shapes of the crystallites, and also their conductivity; I/V measurements show that the islands, as well as the substrate, have good metallic conductivity.

It is worthwhile noting that steps corresponding to both the Mo(110) and (100) surfaces (2.23 and 1.57 Å in height) could be identified. This is indeed a strong indication that the islands actually consist of Mo. Other possibilities such as pure Si or any one of the stable Mo silicides [$MoSi_2$, Mo_5Si_3, or Mo_3Si (Ref. 5)], would not be expected to have this kind of step height. Moreover, Si crystallites would not show metallic conductivity, the more Si-rich silicides do not have a cubic crystal structure as seems to be the case here, and Mo_3Si islands would most likely show a more epitaxial character.

The orientation of the crystallites with respect to the substrate is not always the same, but on several occasions they can be identified as having the (100) plane parallel to the substrate, in which case the equilibrium shape of the bcc crystal[8] can be recognized; see Fig. 2(b). It has thereby been found that the [100] directions of the Mo crystallites have an angle of 53°±5° with respect to the substrate [100] direction. This is close to the substrate $[\bar{1}11]$ direction (54.8° from [100]), a direction that coincides with the close-packed direction for the substrate Si atoms; see Figs. 3(a) and 3(b), which display the $A15$ unit cell and the Si-terminated (110) surface. There is not a perfect match in the atomic structure of the substrate and the

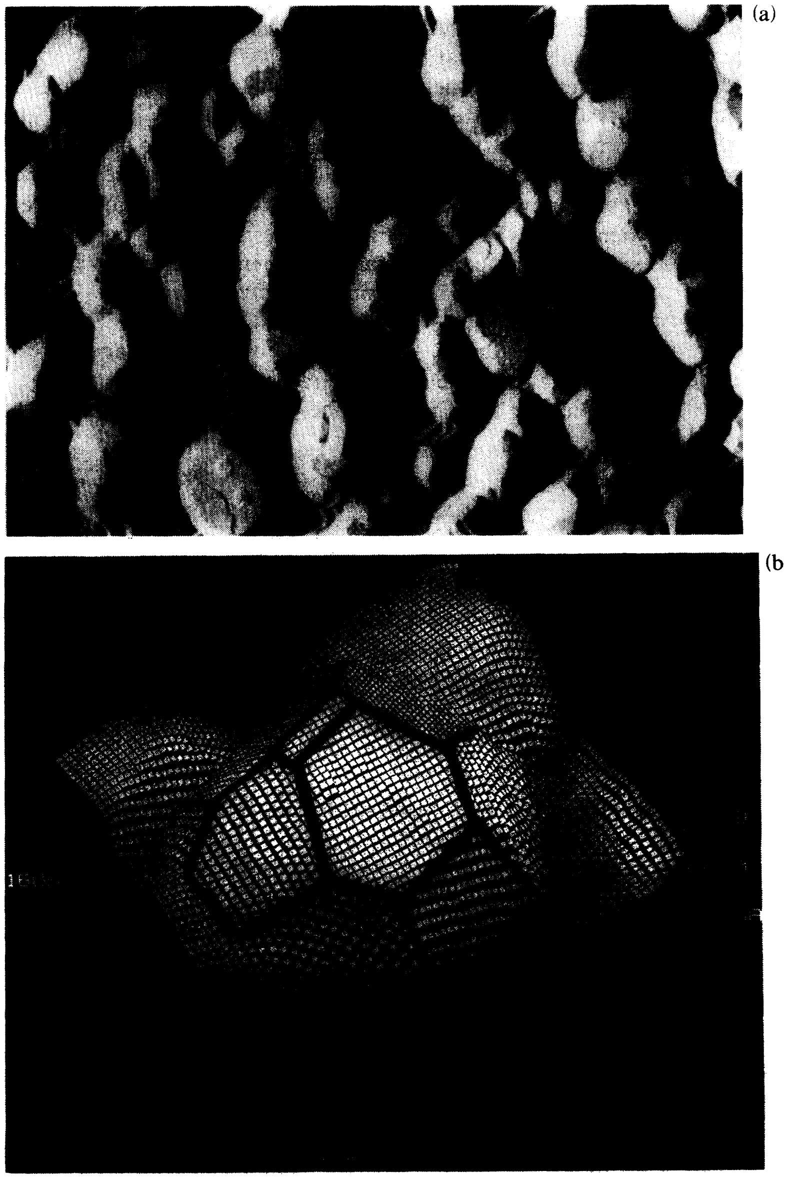

FIG. 2. (a) A large-scale (200×1600 $Å^2$) overview image of the Mo_3Si surface. The crystallinelike islands are thought to consist of pure bcc Mo. Note also the well-ordered substrate surface visible between the islands. The tunneling bias was 0.4 V (sample voltage) and the current setting 1.0 nA. (b) An enlarged part of the image showing an individual crystallite, where the equilibrium shape of a bcc crystal can be recognized.

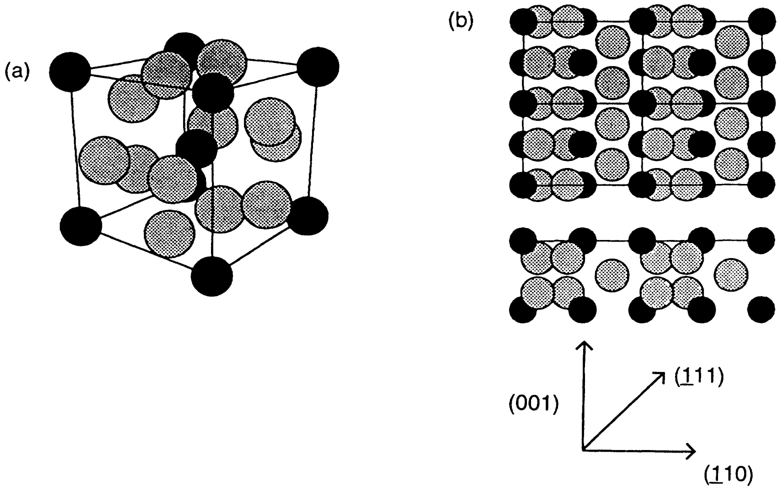

FIG. 3. (a) Depiction of the *A* 15 unit cell. The open circles represent metal atoms (Mo or Cr), and the filled circles represent Si atoms. (b) Top and side view of a Si-terminated (110) surface.

crystallites, but one may speculate that the rows of Si atoms can serve as a guide for the overlayer Mo atoms.

The obvious question to address now is why these Mo crystallites are formed, and why a similar thing does not happen on the Cr_3Si surface. It is well known that the surface chemical composition of an alloy can differ considerably from the bulk composition. This can be due to thermal segregation or preferential sputtering during the sample preparation process. In this case, for an ordered alloy structure, the phenomenon of surface segregation is not likely to be significant.[9] On the other hand, large differences in preferential sputtering between these silicides can actually be predicted. The relative sputtering rates in a binary compound will depend on the masses of the involved components, but also on other factors such as the surface binding energies.[10–12] The mass differences would favor a selective sputtering of Si in both cases, although the effect would be expected to be more pronounced in the case of Mo_3Si. The surface binding energies are not directly accessible, but it has been shown that they, for the purpose of simulating preferential sputtering effects in binary compounds, can be estimated in simple approximations from tabulated thermodynamical data.[10] The surface binding energies of a binary alloy *AB*, where *B* is depleted at the surface, are thereby defined as

$$\begin{aligned} E_A &= \Delta H_{As} , \\ E_B &= \Delta H_{Bs} + \Delta H_f , \end{aligned} \tag{1}$$

where $\Delta H_{A,Bs}$ denotes the sublimation enthalpies of the pure components and ΔH_f the heat of formation of the compound *AB*. Here relevant literature data for these quantities reads $\Delta H_s(\mathrm{Mo})=657$, $\Delta H_s(\mathrm{Cr})=395$, $\Delta H_s(\mathrm{Si})=415$, $\Delta H_f(\mathrm{Mo_3Si})=29$, and $\Delta H_f(\mathrm{Cr_3Si})=23$ kJ/mole.[13,14] In the case of Mo_3Si the situation seems quite clear; both the mass difference and the surface binding energies point towards a selective sputtering of Si, and an enrichment of Mo on the surface would be expected, as is also observed. It can be believed that the sputtering leads to a Mo-rich surface, and that the crystallites are formed upon annealing. For Cr_3Si the situation is more complicated, the difference in mass between the components is smaller, and the enthalpies of sublimation are quite close. It is not obvious which component will be depleted at the surface, and how Eq. (1) should be used. Possibly the two contributions for a preferential sputtering, difference in mass and surface binding energies, more or less cancel each other, leading after annealing to the well-ordered surface in Fig. 1.

For both surfaces the measured step heights between terraces correspond well to $a/\sqrt{2}$, where a is the lattice constant of 4.90 and 4.56 Å, respectively.[5] This would be expected if a pure Si or metal termination is assumed. For the Mo_3Si surface the steps were found to run preferentially in the [001] direction with sharp well-defined edges, whereas the step directions on the Cr_3Si surface showed no preferential orientation with respect to the underlying lattice. Another noticeable difference between these surfaces concerns the resolution on the terraces. While atomic resolution was readily obtained on the Mo_3Si surface, this could never be observed on the Cr_3Si surface. In this case the tunneling conditions were considerably less stable, and the noise level prevented any observations of atomic features. This was regardless of the chosen tunneling parameters, with voltages and current settings in the ranges ±0.0001–3 V and 0.1–5 nA, respectively.

Figure 4 shows a high-resolution STM image of the $Mo_3Si(110)$ surface. Atomiclike features appear as bands of zigzag chains running over the surface. The corrugation amplitude along these bands was found to be highly dependent on the tip structure, but at most ≈0.6 Å. As this is a metallic surface, the observed maxima can be believed to resemble the positions of the outermost atomic positions to a good approximation.[15] A comparison with the atomic-structure models in Fig. 3 reveals that these maxima would coincide well with the topmost atomic positions for a Si-terminated surface, as depicted in Fig. 3(b). The appearance of the bands can be understood considering the structure of the Mo sublattice. An unreconstructed Mo-terminated surface would not give this kind of surface atomic structure. Removing the topmost Si atoms in Fig. 3(b) would lead to zigzag chains of Mo atoms, but these chains would have a different symmetry with larger open angles. The rows are more narrow and the atoms do not align with the (111)-type directions.

We thus conclude that the Mo_3Si surface is Si terminated, in agreement with the earlier photoemission study.[3] Does this also hold for the $Cr_3Si(110)$ surface? As previously mentioned, the measured step heights indicate that it is either Si or Cr terminated, but there is no atomic resolution and the tunneling conditions appear drastically different in this case. Assuming a Si-terminated surface this difference would be quite surprising. These systems have closely related electronic configurations, and one would naively expect similar STM images. A possible explanation is that this surface contains metal atoms in the topmost layer. This could also explain the different characters of the steps, with much more well-defined directions on the Mo_3Si surface. In addition it would seem consistent with the assumption of a lower surface binding energy for Cr than for Si to explain the absence of preferential sputtering in this case. In a simple picture one would expect the element with the lower surface binding energy to reside on the surface.[16]

The previous photoemission studies of these surfaces indicated Si termination in both cases,[3,4] which thus contrasts to the above suggestion of a Cr toplayer for $Cr_3Si(110)$. It can also be noted that the sensitivity of the photoemission studies was not sufficient to detect the Mo crystallites on the Mo_3Si surface. A problem here is that the Cr $3p$ and Mo $4p$ components have very large intrinsic widths, leading to obvious difficulties in identifying surface-related shifts. It can thus be questioned to what extent information on the terminating layer can be extracted from such core-level data. The mere observation of surface shifts of the Si $2p$ component, or even the adsorption experiments, may not be sufficient to exclude the possibility of Cr atoms in the surface layer. An interesting extension of the core-level spectroscopy work would, in this respect, be to investigate instead the Cr $2p$ and/or Mo $3d$ levels, or to undertake a more quantitative analysis of the diffraction effects discussed in these papers.[3,4] One may however note that the very different surface-to-bulk intensity ratios of the Si $2p$ component, as compared between the cases of Mo_3Si and Cr_3Si, actually would be well explained by the presence of metal atoms in the terminating layer of the Cr_3Si surface.

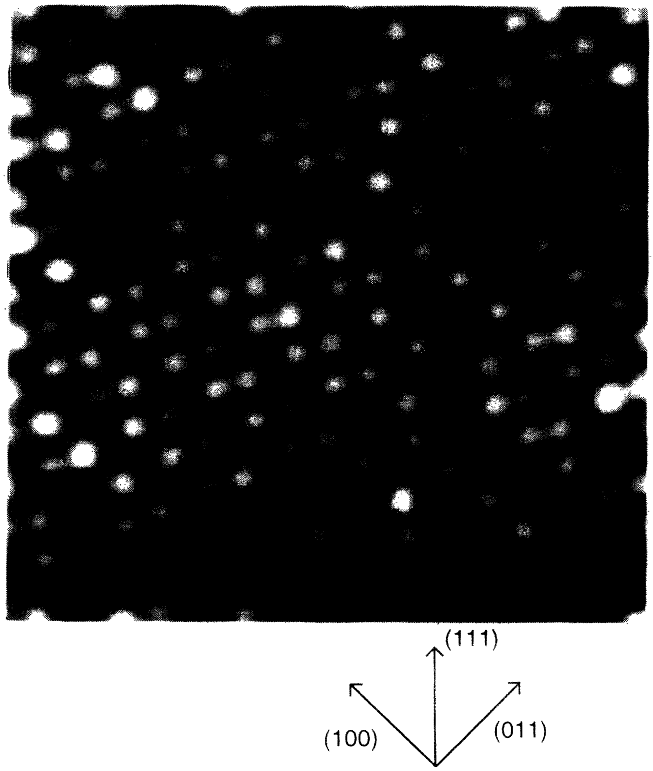

FIG. 4. An atomically resolved image of the $Mo_3Si(110)$ surface. It is suggested that the maxima correspond to top-layer Si atoms, see text. The tunneling voltage was 10 mV and the current setting was 1.0 nA.

To summarize, we have applied STM to study the morphology and atomic structure of $Mo_3Si(110)$ and $Cr_3Si(110)$ bulk-silicide surfaces after sputtering and annealing. Large differences concerning both morphology and possibly also the nature of the topmost atomic layers have thereby have been found. Differences in preferential sputtering effects have been discussed, and it was suggested that these can explain the fact that metal crystallites are formed on the Mo_3Si surface but not the Cr_3Si surface. It was shown that the Mo_3Si surface most probably is terminated by a pure Si layer. It could not be verified if this also holds for the Cr_3Si surface, but in contrast to a previous photoemission study[4] it is argued that this surface might be metal terminated instead.

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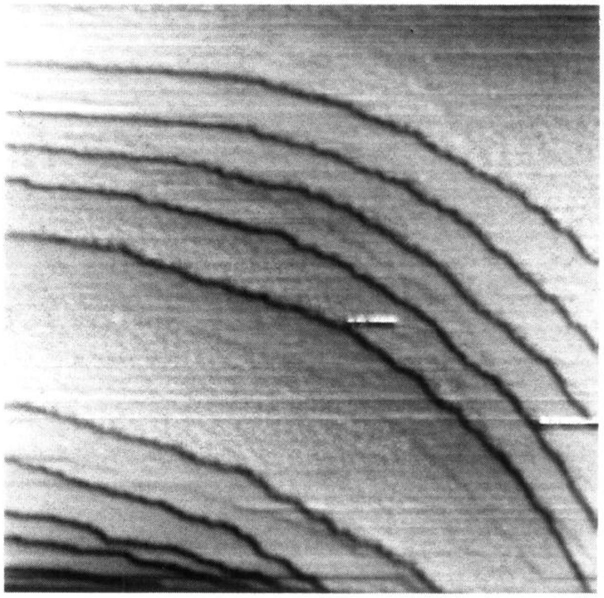


FIG. 1. A large-scale (2000×2000 Å^2) overview image of the Cr_3Si surface. The tunneling bias was 0.4 V and the current setting 1.0 nA.

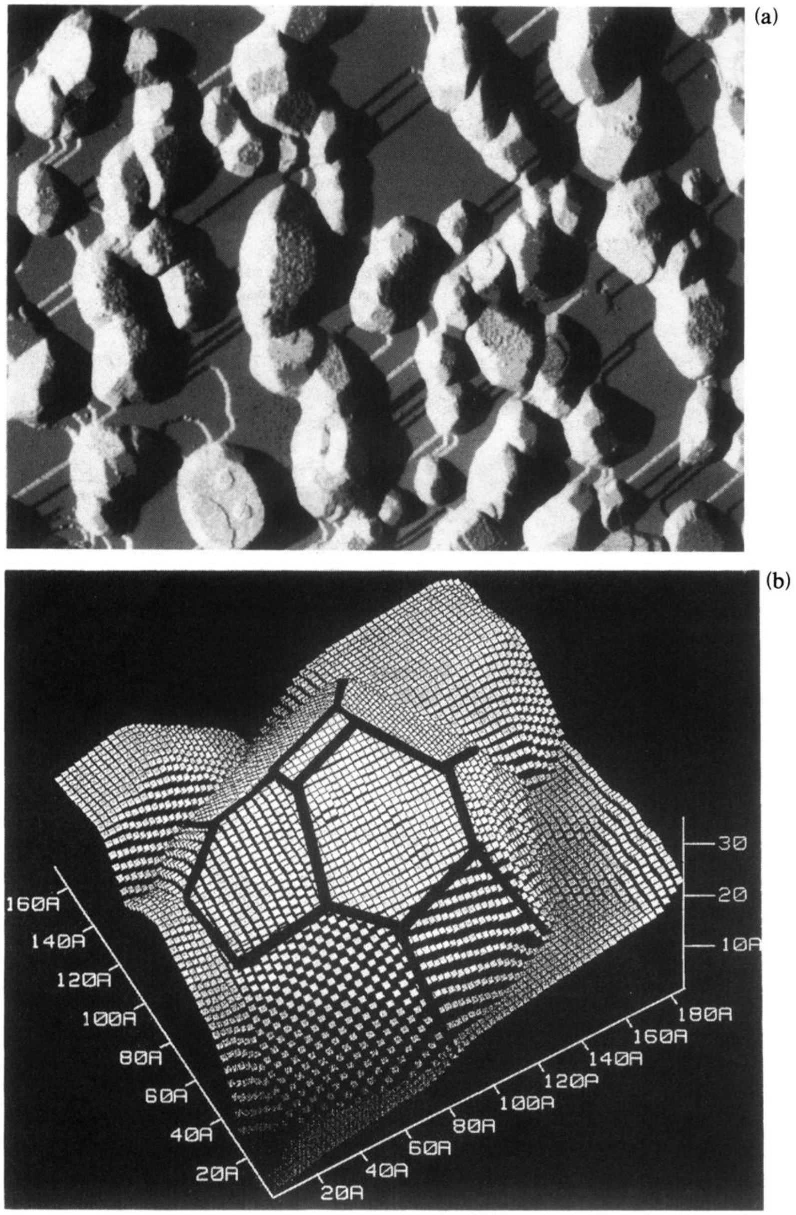


FIG. 2. (a) A large-scale (200×1600 Å^2) overview image of the Mo_3Si surface. The crystallinelike islands are thought to consist of pure bcc Mo. Note also the well-ordered substrate surface visible between the islands. The tunneling bias was 0.4 V (sample voltage) and the current setting 1.0 nA. (b) An enlarged part of the image showing an individual crystallite, where the equilibrium shape of a bcc crystal can be recognized.

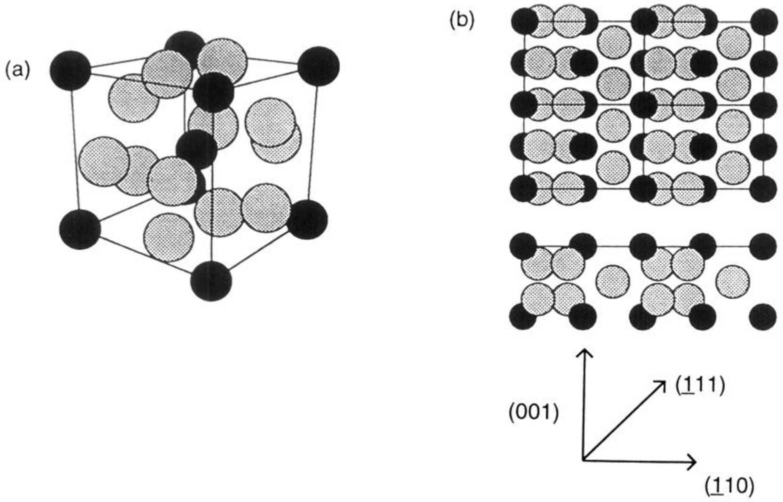
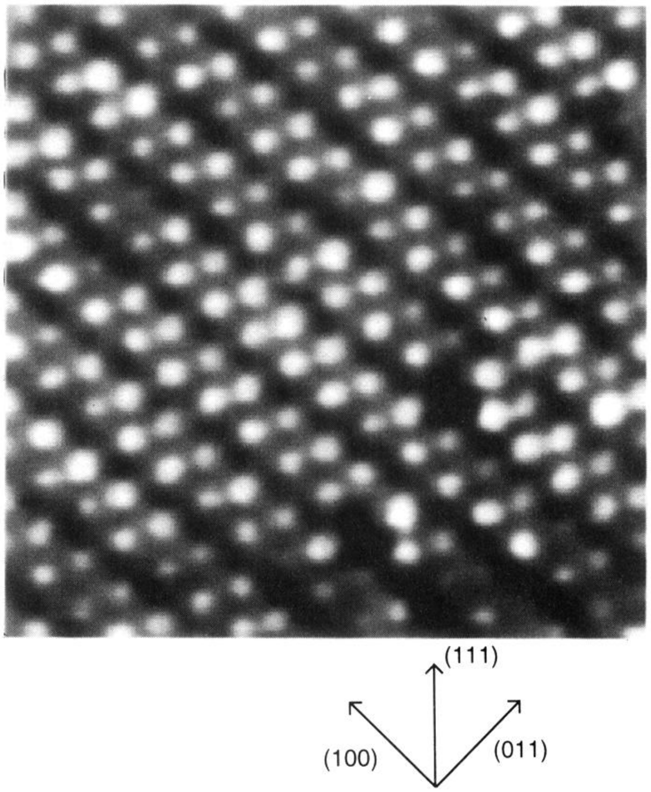


FIG. 3. (a) Depiction of the *A*15 unit cell. The open circles represent metal atoms (Mo or Cr), and the filled circles represent Si atoms. (b) Top and side view of a Si-terminated (110) surface.



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