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Metal-silicon interfaces and multiple scattering in their low-energy electron diffractions

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After carefully analyzing many interesting experimental phenomena observed with low-energy electron diffraction (LEED) in a series of recent studies on early stages of the formation of many metal-silicon interfaces (Ta/Si, V/Si, Ni/Si, Pd/Si, Pt/Si, Ag/Si, Al/Si), we conclude that all these interfaces, which are defined here as being directly connected to the silicon, have a unique atomic structure—common interfacial phase, and that this structure produces only kinematic LEED intensity spectra.

I. INTRODUCTION

Metal-silicon interfaces have been of fundamental scientific interest for about half a century. In addition, because of the technological importance of such interfaces, in recent years, the study of the chemical, structural, and electronic nature of these interfaces has been greatly intensified.[1,2]

It seems to be universally accepted that many metals form so-called reactive interfaces with silicon at room temperature. Of these are some noble metals such as Au (Refs. 3—5) and Cu, (Refs. 6 and 7) some near-noble metals such as Ni (Refs. 8—13) and Pd, (Refs. 8, 14, and 13) and some refractory-transition metals such as Cr (Refs. 15 and 16) and Ti (Ref. 17). But the implication of "reactive interfaces" is not clear, except for there being some strong chemical reactions and an intermixing tendency. Do these interfaces have any common characters or are they really "of distinctly different quality"?[13]

Perhaps it is also generally accepted that some metals such as Ag, (Refs. 18—20) V, (Ref. 21) and Ta (Ref. 22) form so-called nonreactive interfaces with silicon at room temperature. Again, the meaning of "nonreactive interfaces" is not clear. It may only mean that there is "no substantial mixing" (Refs. 20 and 23). Then, naturally, one may ask if there is indeed any clear-cut difference between the reactive and nonreactive interfaces. In fact, at temperatures higher than room temperature, strong intermixing does occur at nonreactive metal-silicon interfaces.[21,22] This indicates that it is only a matter of temperature that discriminates the nonreactive interfaces from the reactive ones. But we see no reason for setting room temperature as the margin.

The cause of the ambiguous situation mentioned here is twofold: The products of the metal-silicon reactions are very complicated, and the definition of the metal-silicon interfaces itself has never been clear (or there might be no definition at all). To escape from such a situation, in this work we use the term "metal-silicon interface" with the understanding that it is something which is not the clean original silicon but is connected directly to the clean original silicon.

Based on this understanding of the interfaces, LEED is a very suitable technique for monitoring the interface formation processes, especially their early stages. To catch the interfaces before they sink to levels too deep to be detected with LEED, in general, the experiments consisted in depositing a few monolayer equivalents of a given metal at a deposition rate ranging from 0.1 to 1 monolayer/min. on a clean surface, at room temperature or somewhat higher. The structural changes were monitored with LEED intensity spectra.

In this paper, we have analyzed those experimental results and phenomena of our recent works[24,25] that look somewhat curious and have no relationship to one another and have found a unified explanation of those phenomena.

II. LEED OBSERVATIONS

To facilitate the discussions in Sec. III, we summarize the important experimental facts of our recent works[24,25] here.

(i) All metals considered here (Ag, Al, Ni, Pd, Pt, Ta, and V), deposited at room temperature on Si(111)7×7, modify the surface structure to an α-7×7 structure.[24] The resulting α-7×7 structure is the same for all the metals, except Al, which does modify the 7×7 structure to the α-7×7 structure but not completely. The modification is evidenced by two major changes in the LEED pattern: increased background and extinction of some (usually small) peaks in the intensity spectra of integral-order beams, although symmetry and periodicities remain those of the 7×7 structure (see Fig. 2 of Ref. 24).

(ii) After high-temperature anneals, the Ni-, Pd-, Pt- and Ti- deposited Si(111) surfaces ultimately become a 1×1 structure.[24] The LEED intensity spectra indicate that this structure is essentially the same for all metals involved here and is practically identical to the so-called "quenched 1×1" structure discussed elsewhere.[26] Further depositions of the same metals on the 1×1 structure at room temperature modify the structure to an α-1×1 structure which has higher background and somewhat different LEED intensity spectra, the difference being again the extinction of some small peaks (Fig. 1).

(iii) Further depositions of Ag on the Si(111)3×1-Ag surface modify the surface to an α-3×1-Ag structure, with similar modification to those mentioned above.[24]

(iv) Depositions of Ni on a clean Si(001)2×1 surface

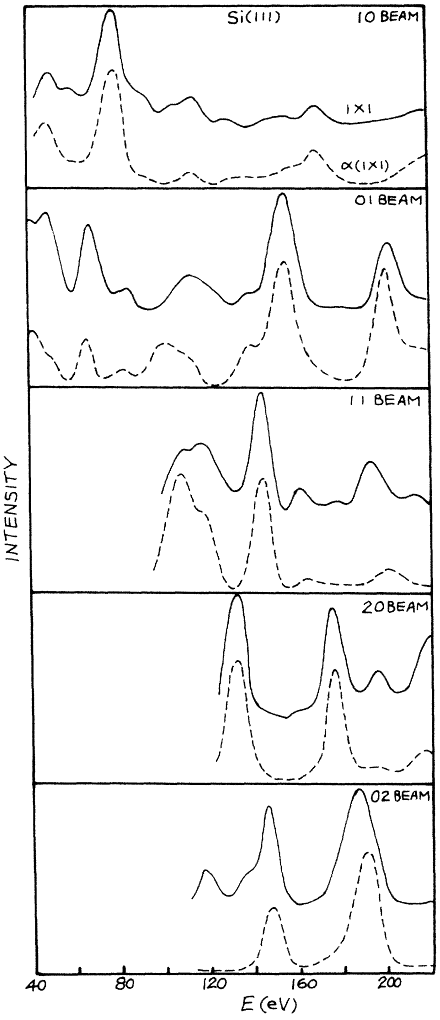

FIG. 1. LEED intensity spectra of the 1×1 structure and α-1×1 (see text) structure of the Si(111) surface (Ref. 24).

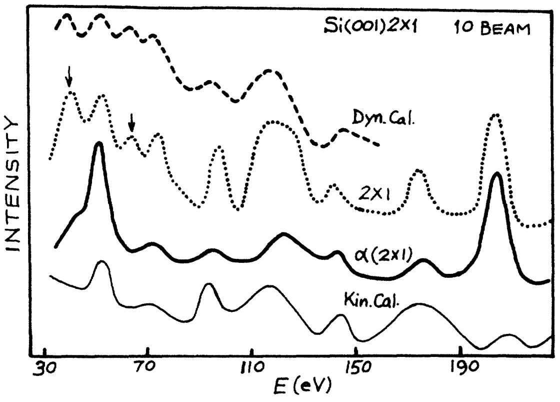

FIG. 2. LEED 10 intensity spectra of the Si(001) surface. Dotted curve: experimental curve from the 2×1-reconstructed structure. Thick solid curve: experimental curve from the α-2×1 (see text) structure. Dashed curve: dynamically calculated curve of our Si(001)2×1 model (Ref. 30). Thin solid curve: kinematically calculated curve of the same model (Ref. 25).

modify the surface to an α-2×1 structure[25] in a way similar to that of the above three cases. Figure 2 shows the 10 beam intensity spectrum (not normalized) of both structures. The differences between the two are not very significant: There are two more peaks (indicated with arrows) on the 2×1 spectrum than on the α-2×1 spectrum.

(v) Surprisingly, further depositions of Ag at a rate of 0.5 monolayer/min. on the Si(111)$\sqrt{3}\times\sqrt{3}$-30°-Ag ($\sqrt{3}\times\sqrt{3}$-Ag) surface at room temperature did not cause any changes, neither in the intensity spectra nor in the background, even when the total Ag coverage was as high as 16 monolayers.[24]

(vi) Another puzzling fact is that the $\sqrt{3}\times\sqrt{3}$-Ag and the $\sqrt{3}\times\sqrt{3}$-Ta surfaces have almost identical intensity spectra (see Fig. 3 of Ref. 24), and both have sharp spots on a low background.[24]

III. DISCUSSION

A. The metal atoms location

Since in the first four cases of the preceding section the background of the patterns increase more or less, no doubt, at least part of the atoms of metals deposited form disordered overlayers. The question here is where are those metal atoms that are responsible for the modifications of the LEED intensity spectra?

It seems to us that those metal atoms together with the silicon atoms could not form interface structures other than the eight shown in Fig. 3. It will be clear, after the following considerations, that only the eighth structure is the real one.

(i) The interfaces could not be of disordered overlayers on top of the original surfaces, since disordered overlayers do not change the LEED intensity spectra of their substrate but lower the overall intensities. Figure 4 shows such an example from Ref. 27.

(ii) The interfaces could not be of incommensurate ordered overlayers on top of the original surfaces, since incommensurate ordered overlayers also do not change the intensity spectra of their substrate. Figure 5 gives such an example from Ref. 28.

(iii) The interfaces could not be of commensurate ordered overlayers on top of the original surfaces, since a

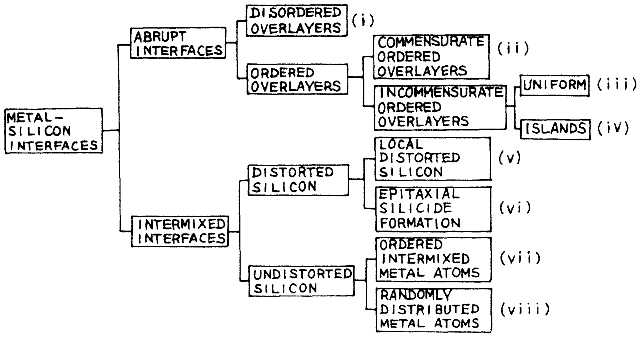

FIG. 3. Classification of all possible metal-silicon interface structures.

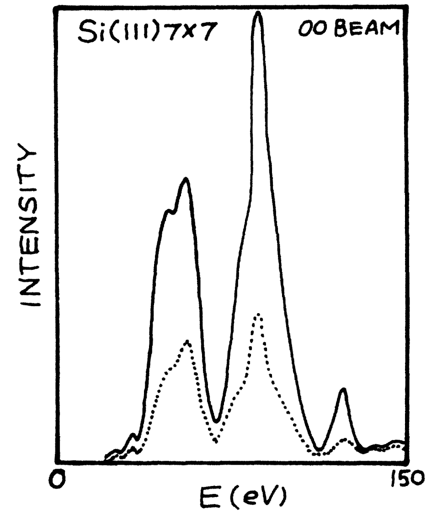

FIG. 4. LEED intensity spectra from a very well-ordered clean Si(111)7×7 surface (solid curve), and the same surface after a silicon amorphous overlayer of a thickness of 1.2 monolayers which had been deposited at room temperature (dotted curve) (Ref. 27).

commensurate ordered overlayer or even submonolayer can cause the intensity spectra of the system to be *significantly* different from those of the original surfaces. Figure 6 is an example of such a case from Ref. 29.

(iv) The interfaces could not be of islands (incommensurate) on top of the original surfaces. According to what has been mentioned in (ii), such types of structures should not change the intensity spectra of the original surfaces, whereas in the first four cases of the preceding section the depositions did change these spectra.

(v) Recently, Clabes[13] has suggested that depositions of near-noble metals may cause some local destructive effects on silicon surface reconstructions. Meanwhile, Clabes [13] has concluded that the interaction of Ni with the Si lattice is of a distinctly different quality than in the case of Pd. Therefore, one must conclude that if some local destructive effects were responsible for the formation of the α-7×7 structure (or the α-1×1 structure), the structure should not be the same for Ni as for Pd. However, the fact is that the α-7×7 structure (or the α-1×1 structure) is practically identical for all metals tested here. Thus, we must conclude that the modifications to the original surfaces caused by depositions of the metals are not results of some local destruction of the original surface reconstructions.

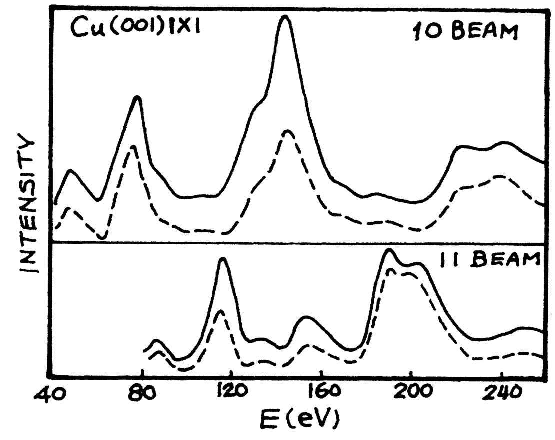

FIG. 5. LEED intensity spectra from a clean Cu(001) surface (dashed curves), and the same surface covered with incommensurate Nb layers (solid curves) (Ref. 28).

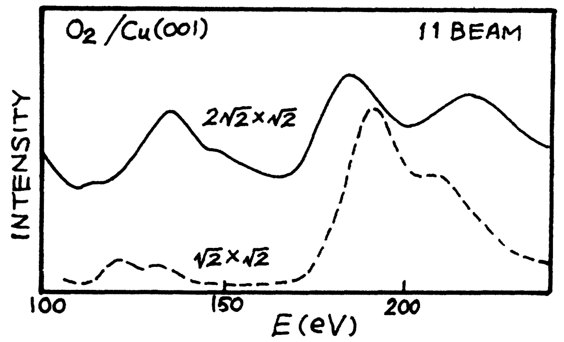

FIG. 6. LEED 11 spectra of Cu(001) with different oxygen coverages (both less than 1 monolayer), thus, different patterns. The Cu surface structures and the binding geometry of the oxygen on the surfaces are the same in the two cases (Ref. 29).

(vi) It is difficult to believe that the atoms of the metals reacting with silicon form uniform silicides. This is quite clear, since in *all* of these cases for *all* of the metals involved here, the symmetry of the patterns is not changed by depositions.

(vii) It is impossible for the atoms of the metals intermixing with silicon atoms to form ordered structures with the same symmetry as that of the original surfaces. If they resulted in forming such ordered structures, since atoms of different metals have different scattering properties, the α-7×7 structure (or the α-1×1 structure) of different metals should have different, instead of identical, intensity spectra.

(viii) Now, we see the only possibility as being, that after diffusion towards the interior, the atoms of the metals deposited occupy randomly the interstitial voids of the almost undistorted silicon lattice, as suggested by many works, such as Refs. 3 and 10. We will discuss below how such structures can be responsible for the experimental phenomena described in Sec. II.

B. The very kinematic character of the LEED intensity spectra from the metal-silicon interfaces

We see in Fig. 2 that the dynamically calculated (dashed) curve of our Si(001)2×1 model[30] matches the experimental (dotted) curve from the clean Si(001)2×1 surface, and the kinematically calculated (thin solid) curve of the same model matches the experimental (thick solid) curve from the α-2×1 structure. This indicates strongly that the depositions of Ni eliminate the multiple-scattering peaks (indicated with arrows) from the LEED intensity spectra, thus making the spectra from the α-2×1 structure very kinematic.

We should not claim that the α-1×1 structure of the

Si(111) surface will also produce only kinematic LEED intensity spectra until we can find a model for the α-1×1 structure which has its kinematically calculated spectra matching the experimental spectra from the surface. In fact, we have found such a model[31] for the structure. Therefore, we conclude that the LEED intensity spectra of the α-1×1 structure are also kinematic.

We have mentioned that the depositions of Ag on the $\sqrt{3}\times\sqrt{3}$-Ag surface do not modify the surface at all. If we assume that depositions of the metals involved here on silicon surfaces always eliminate multiple-scattering peaks from LEED intensity spectra, we must conclude that the LEED intensity spectra of the original $\sqrt{3}\times\sqrt{3}$-Ag structure contain no multiple-scattering peaks. In fact, we have solved this surface structure[32] with a kinematic scheme kinematic low-energy electron diffraction/orthogonal experimental design (KLEED/OED),[33] and thus have proved this assumption, as well as the assumption that the $\sqrt{3}\times\sqrt{3}$-Ag structure we tested was kinematic in LEED intensity spectra. However, if we hope to unify the denominations such that all surfaces that produce only kinematic LEED intensity spectra are given a letter α to their notations, we have to denominate this surface as α-$\sqrt{3}\times\sqrt{3}$-Ag, instead of the $\sqrt{3}\times\sqrt{3}$-Ag. One may ask if the $\sqrt{3}\times\sqrt{3}$-Ag surface is possible. We suppose that had we deposited less Ag than we did in preparing the surface, as some workers[34] did, we might have gotten the $\sqrt{3}\times\sqrt{3}$-Ag surface. But at this stage, we cannot deny that only the α-$\sqrt{3}\times\sqrt{3}$-Ag is possible.

Since the α-$\sqrt{3}\times\sqrt{3}$-Ag structure has the same character as the α-1×1 and α-2×1 structures do in the sense that they both produce only kinematic LEED intensity spectra, it is reasonable to predict that the α-$\sqrt{3}\times\sqrt{3}$-Ag structure has also some metal atoms (Ag) occupying randomly the interstitial voids of its silicon substrate. However, the low background of the LEED pattern of this structure seems to be somewhat in contradiction with the random distribution of the Ag atoms. But a single-scattering simulation[35] over an absolutely disordered system has shown that, in contradiction to what is intuitively expected, such systems do not result in a high background.

Since we are far from having the α-7×7 structure solved, at present, we cannot prove directly that the structure produces only kinematic LEED intensity spectra. However, we see from Sec. II that this structure is in every sense similar to the α-1×1 structure, except that it has a different surface reconstruction. Thus, there should be no risk in concluding that the α-7×7 structure also produces only kinematic LEED intensity spectra.

Since depositions of Ag on the Si(111)3×1-Ag surface modify the 3×1 structure to the α-3×1 structure, the latter ought to be kinematic in LEED intensity spectra. Its surface structure should be solvable with kinematic calculations comparing with the α-3×1 experimental LEED intensity spectra, but this has not yet been done.

Let us now proceed to a different but closely related question: How do we understand the resemblance between the LEED intensity spectra from the α-$\sqrt{3}\times\sqrt{3}$-Ag and α-$\sqrt{3}\times\sqrt{3}$-Ta surfaces? There should be no doubt that they must have almost identical atomic structures. But the full dynamic LEED calculations[36] of the same models for the two surfaces gave intensity spectra with significant differences between them. Therefore, once again we logically reach the conclusion that the two surfaces are not dynamic in terms of LEED. Naturally, one may ask why in the single-scattering cases the different scattering properties of Ag and Ta do not result in significantly different LEED intensity spectra, while in the multiple-scattering cases they do. We think the answer to the question is twofold: Firstly, in the single-scattering cases the atomic scattering factor $f(\theta)$ is involved only once, while in the multiple-scattering cases it is involved for two or more times. Secondly, in the single-scattering cases the scattering angle θ, because of the backscattering geometry, may take only values close to 180°, while in the multiple-scattering cases, θ may take values from 0° to 180°. The differences between $f(\theta)$'s[37] of different elements are relatively smaller for θ's close to 180° than for θ's of other values.

C. Common interfacial phase

Sections III A and III B indicate that when atoms of a given metal are deposited on a silicon surface at or near room temperature, at least some of them can diffuse towards the interior and occupy randomly the interstitial voids of the essentially undistorted silicon lattice. The structure thus formed produces only kinematic LEED intensity spectra.

We check the validity of this statement again. The systems we have tested are of reactive interfaces (Ni/Si, Pd/Si, Pt/Si) as well as of nonreactive interfaces [Ag/Si, Al/Si, V/Si, and Ta/Si (at about 500 °C)]. The statement is valid to *all* of these systems, except that Al is weaker in eliminating multiple-scattering peaks.

For a given system, such as the Ni/Si, the statement is valid to *all* substrate orientations tested (001) and (111). For a given orientation, say the (111) one, the statement is valid to *all* surface reconstructions, such as the 7×7 and 1×1 ones as well as the $\sqrt{3}\times\sqrt{3}$-Ag and 3×1-Ag ones. Furthermore, the character exhibited in producing only kinematic LEED intensity spectra is rather stable against moderate anneals, even when the anneals may change surface reconstructions. For example, the α-7×7-Ag and α-3×1-Ag structures upon annealing at about 600 °C yield the α-$\sqrt{3}\times\sqrt{3}$-Ag structure.[24] According to points discussed above, this means that the status of the metal atoms that randomly occupy the interstitial voids of the silicon lattice remains unchanged upon annealing, as long as the anneals do not cause significant desorption of the metal atoms.

We now inevitably introduce the concept of a common interfacial phase to specify the metal-silicon interfaces. At present the content of this concept is the following. (i) The metal-silicon interfaces, formed with depositions of any metal (mainly the transition metals and the noble metals) at a low deposition rate on a silicon surface of any orientation with any surface reconstruction at or near room temperature, have a unique atomic structure—the common interfacial phase. (ii) In this phase the metal atoms occupy randomly the interstitial voids of the almost undistorted silicon lattice. (iii) A previous result[38] has shown that in this phase the atomic ratio of metal to silicon is approximately 1:6. (iv) This phase is stable against anneals, as long as the anneals do not cause significant desorption of the metal atoms. (v) This phase produces only kinematic LEED intensity spectra.

Although the concept of a *common* interfacial phase is brand new, Bisi, Chiao, and Tu[12] had explicitly introduced a concept of interfacial phase to their study on Ni/Si(001) and Ni/Si(111) interfaces. The characteristics of the interfacial phase in their work are very similar to those of the common interfacial phase in this work. Besides, some ingredients of the common interfacial phase can be found in many works, such as those of Rubloff *et al.*,[14] Chang and Erskine,[10] Braicovich *et al.*,[3] Cheung and Mayer,[9] and Franciosi *et al.*[15]

D. Why the common interfacial phase produces only kinematic LEED intensity spectra

There should be no doubt that those randomly distributed metal atoms in the silicon lattice are responsible for eliminating or weakening the multiple-scattering peaks on the LEED intensity spectra. But at present we do not know how they do this job.

Nonetheless, we may (and ought to) take advantage of this fact to solve complicated silicon surface structures with kinematic LEED calculations, since multiple scattering is the most serious obstacle in the LEED surface crystallography that causes the LEED to be obstructed in facing the silicon surface structures. As mentioned above, with kinematic LEED calculations, we recently solved the Si(111)$\sqrt{3}\times\sqrt{3}$-30°-Ag structure which we now know has 1 monolayer of Ag and a very deep $\sqrt{3}\times\sqrt{3}$ reconstruction,[32] as well as the Si(111)1×1 structure[24] which we now know has a stacking fault and a very deep oscillatory multilayer relaxation[31] somewhat similar to that of the Si(111)7×7 surface.[33] Based on these works, we believe that tackling the mysterious structure of the Si(111)7×7 surface is no longer unthinkable.

IV. CONCLUSION

The metal-silicon interfaces which are something different from the clean original silicon but connected directly to it, formed by depositions of any of the metals tested here including the refractory-transition metals (Ta and V), the near-noble metals (Ni, Pd, and Pt), the noble metals (Ag) as well as the simple metals (Al), at a low rate of deposition (about 0.1 to 1 monolayer/min.) on a silicon surface of any of the substrate orientations tested with any of the surface reconstructions including the (111)1×1, (111)7×7, (001)2×1, (111)$\sqrt{3}\times\sqrt{3}$, and (111)3×1 ones at or near room temperature, have a unique atomic structure—the common interfacial phase which has the following features. (i) The metal atoms randomly occupy the interstitial voids of the essentially undistorted silicon lattice. (ii) In this phase the atomic ratio of metal to silicon is about 1:6. (iii) It is stable against the moderate anneals that do not cause significant desorption of the metal atoms. (iv) It produces only kinematic LEED intensity spectra.

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