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The deposition of silicon on metal single-crystal surfaces, studied by RAIRS, LEED and AES

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Abstract. We report here low-energy electron diffraction (LEED), Auger electron (AES) and reflection–absorption infrared spectroscopic (RAIRS) studies of the adsorption of disilane (Si_2H_6) on the hexagonal Ru(0001) surface at room temperature. Initial steps show the formation of an adsorbed SiH fragment which is easily decomposed to leave elemental silicon at 450 K. The room temperature LEED patterns show a coverage dependence, with a transition from a (2 × 2) pattern at low coverage to a mixed (2 × 2) and (1.5 × 1.5) pattern towards saturation. Annealing of the saturated surface to 800 K results in the formation of an ordered overlayer with a (3 × 3) R18 LEED pattern which, in combination with AES data, is assigned to an incommensurate layer of ruthenium silicide.

1. Introduction

The infrared (IR) spectroscopy of silicon growth intermediates from silicon bearing gas-phase precursors such as silane (SiH_4) and disilane (Si_2H_6) is a subject which has yet to achieve the refinement of the vibrational spectroscopy of monolayers on metal surfaces. The application of the reflection–absorption IR spectroscopic (RAIRS) technique to silicon substrates suffers from a number of restricting factors, due principally to the optical properties of dielectric substances. Other IR sampling techniques have been used on silicon surfaces with some degree of success, such as attenuated total reflection (ATR) [1] and transmission IR (TIR) [2]. However, the former of these techniques is limited by substrate absorptions which for silicon occur below about 1100 cm^{-1}, eliminating the silicon hydride deformation modes which occur in the 800–900 cm^{-1} range.

The experimental simplicity of a single external reflection recommends itself as a tool for both basic research and *in-situ* process control. However, we have recently investigated the comparative merits of RAIRS and TIR for adsorbates on silicon [2], in which silicon RAIRS proves to be significantly less sensitive than for metals. Attempts have been made to augment the reflectivity of silicon using multiphase substrates, as in a study of the ATR spectra of Langmuir–Blodgett (LB) films by Yarwood *et al*, in which the reflectivity was artificially increased by the deposition of a metal layer on the upper surface of the adsorbed layer [3], and by McGonigal *et al*, who have demonstrated the advantageous reflectivity of a silicon-on-metal system for single external reflection [4].

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In this article, we report a study of the initial stages of the deposition of silicon on a metal single-crystal surface by RAIRS, LEED and AES, prior to attempts to grow thicker, well ordered silicon films on metals. The system we have chosen is the room temperature adsorption of disilane on a Ru(0001) surface and subsequent annealing. Recently, McCash *et al* [5] have reported the adsorption and decomposition of silane on Cu(100), studied by EELS, AES and RAIRS, in which they observed the deposition of a monolayer of unreactive silicon atoms at low temperature. We have used disilane as a precursor in preference to silane because of its significantly higher reactivity. Sputter-deposition of thin layers of silicon on Ru(0001) monitored by LEED gives patterns in broad agreement with our results [6].

2. Experimental details

The vacuum system consisted of a diffusion pumped circular chamber coupled to a Mattson Instruments Sirius 100 FTIR via KBr optics, described elsewhere [7]. The detector used was a copper-doped germanium photoconductor, liquid helium cooled, covering the 4000–300 cm^{-1} range. Spectra were recorded as the ratio of 1000 clean background scans to 1000 sample scans at a resolution of 4 cm^{-1}. The cleaning procedure involved argon ion bombardment together with high-temperature annealing (1250 K). The substrate cleanness was tested by RAIRS, by adsorbing CO at room temperature and using the characteristic CO stretching frequency of 2061 cm^{-1} for a saturated monolayer at 100 K, with a FWHM of 8 cm^{-1}. This technique is more fully described elsewhere [8]. Disilane (Cambrian Gases) was introduced to the vacuum system via a cured stainless steel gas handling system, and was used without further purification. Mass spectrometry indicated only Si_nH_m fragments and hydrogen. LEED and AES were carried out using a VG 4-grid RFA.

3. Results and discussion

Figure 1 shows the IR and Auger spectra corresponding to a range of cumulative doses up to saturation at approximately 6 L. Although we obtained spectra from 400 to 4000 cm^{-1}, a single band, at 2112 cm^{-1}, is the only feature seen at room temperature. The absence of other vibrations can be most easily explained if this band is assigned to the stretching mode of an SiH bond perpendicular to the surface. This band increases in intensity up to saturation at approximately 6 L with no shift in frequency. Auger electron spectra of the uptake concur with the gradual increase in surface concentration up to a saturation point.

Figure 2 shows the LEED patterns obtained for a clean surface, a low exposure (2 L) and at saturation. The clean surface has a characteristic (1×1) hexagonal pattern which changes to a (2×2) pattern at low coverage. Since the covalent diameter of silicon is larger than the atom spacing of ruthenium in the (0001) plane, and taking the threefold bonding requirements of a single SiH unit into account, the (2×2) pattern can be assigned to the adsorption of such units in alternate threefold hollows, as shown in figure 3. On increasing the exposure, the packing density increases and the pattern partially shifts into a (1.5×1.5) structure. This unusual unit mesh can be best explained as an average pattern, obtained by sliding SiH units closer together. A comparison can be made with CO-coverage-dependent LEED patterns [7], providing

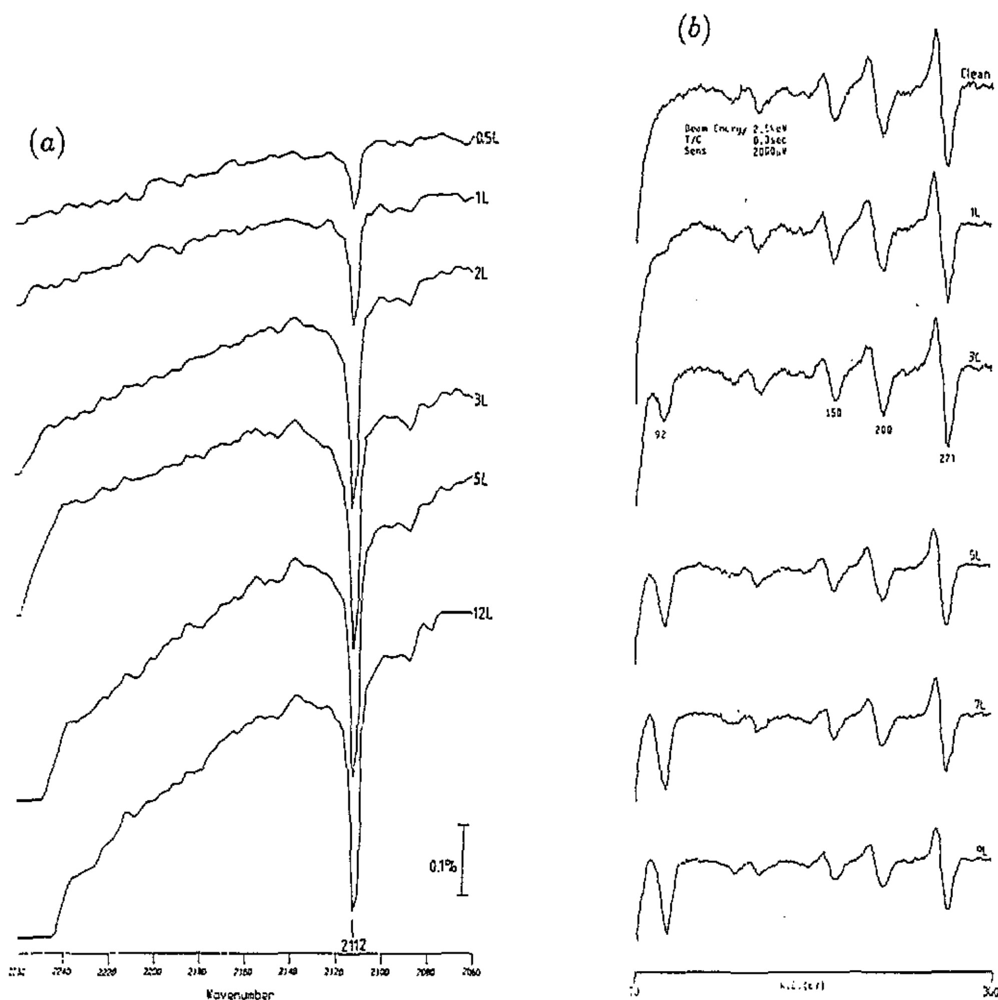

Figure 1. Infrared *(a)* and Auger electron spectra *(b)* of the adsorption of disilane on Ru(0001) at room temperature. The exposures are as measured by ion gauge and are uncalibrated.

that the threefold bonding requirement is borne in mind. Figure 4 shows a possible surface structure with an average (1.5 × 1.5) unrotated unit mesh.

The presence of only SiH units at the surface is taken as evidence that the disilane decomposition, either directly to SiH or via a number of intermediate steps, is extremely rapid at room temperature. Low-temperature adsorption and annealing studies indicate that a variety of fragments are formed below 200 K, but are not stable [9]. On raising the temperature to 400 K, the 2112 cm^{-1} band is lost, but there is no evidence for the loss of silicon from the surface. We are currently investigating the reactivity of these intermediate surfaces.

Annealing the saturated layer to 800 K results in no significant change in the Auger spectrum. However, the LEED pattern (figure 5) shows a complicated mesh of two overlapping structures. Empirical examination shows these unit meshes to be approximately (3 × 3) R18. There is some evidence to suggest that this silicide is not confined to the topmost surface layer, but extends further into the bulk. In a recent

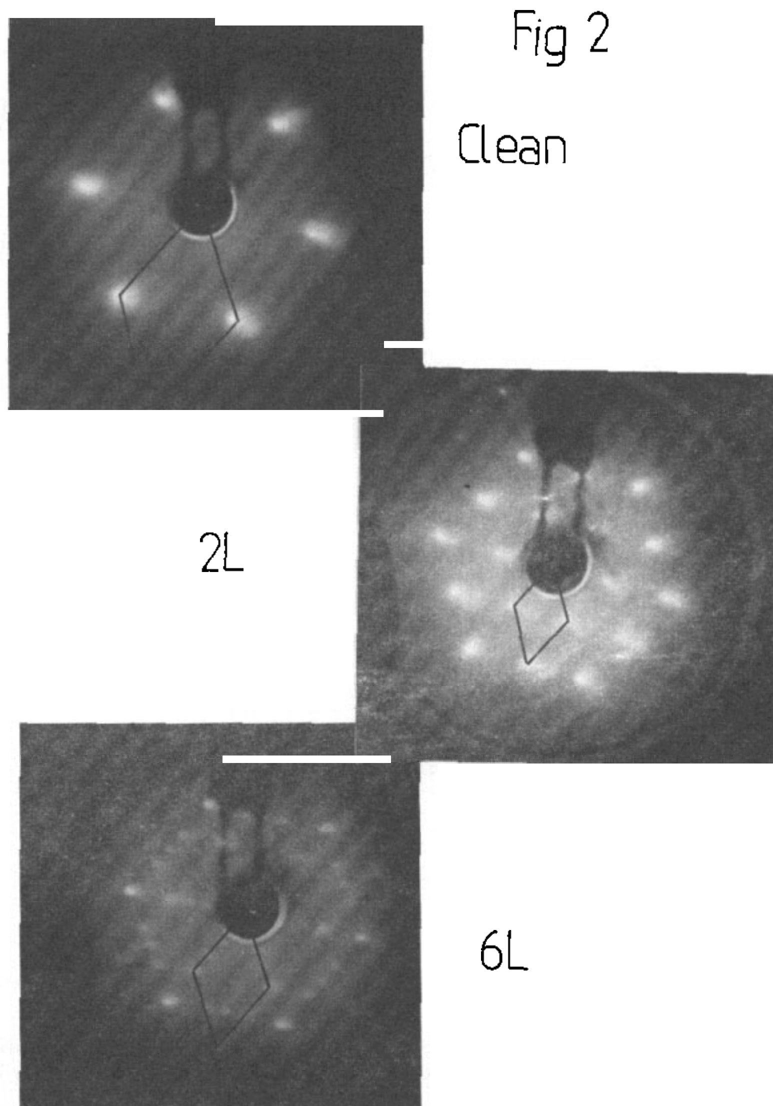

Figure 2. LEED patterns for the clean Ru(0001) surface and during successive exposures to disilane at room temperature. The primary electron energy is 58 eV.

LEED study, Lu *et al* [6] report a similar structure when the silicon layer is deposited by evaporation onto the surface and subsequently annealed. It seems reasonable, therefore, to deduce that this is a stable form of the surface silicide. The complicated LEED pattern is due to this restructured silicide of undetermined stoichiometry, and its registry is not that of an adlayer as seen for the low-temperature deposition, but is that of an incommensurate overlayer. Lu *et al* have described this LEED pattern as $(\sqrt{7} \times \sqrt{7})R\,\mathrm{arctan}\,(\sqrt{3}/5)$ by similar reasoning.

4. Conclusion

The adsorption of disilane at room temperature proceeds via dissociation to form a SiH

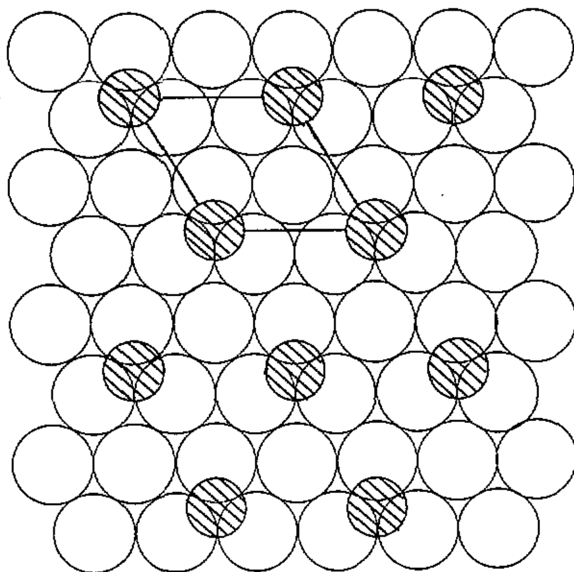

Figure 3. Simplest (2 × 2) surface arrangement with each SiH unit occupying a threefold hollow.

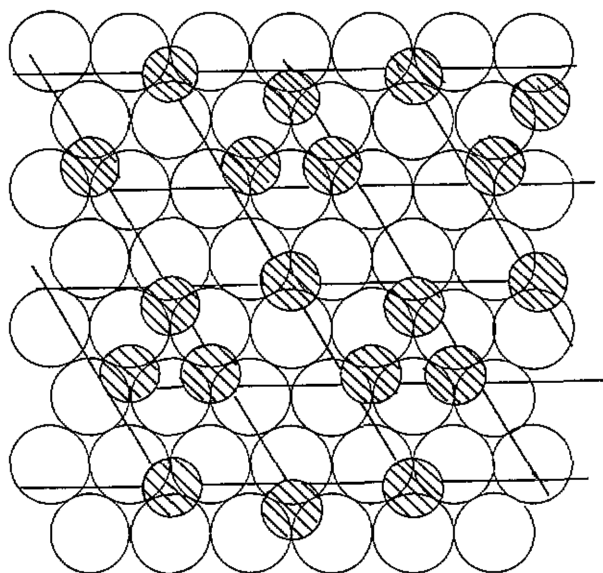

Figure 4. One possible surface arrangement with each SiH occupying a threefold hollow with average unit mesh (1.5 × 1.5).

surface unit which is probably sitting in a threefold site. Coverage-dependent LEED patterns indicate that these units stack together to produce a saturated surface at less than 100% coverage. This surface is unreactive at room temperature and no further disilane will adsorb, despite its high reactivity at this temperature. Annealing to high temperatures leads to further structural changes, with the silicon reacting to produce a layer of ruthenium silicide, which possibly extends some way into the bulk. This layer

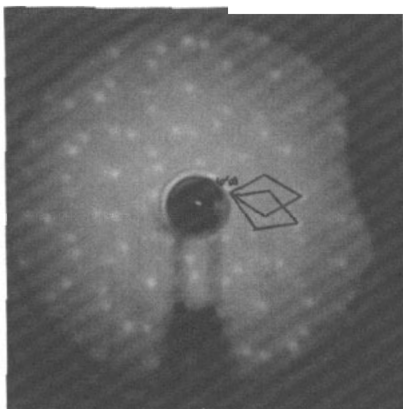

Figure 5. LEED pattern resulting from annealing the saturated surface to 800 K. All the spots can be accounted for in terms of two approximately (3 × 3) meshes roated by 18° in both directions.

is unreactive. At intermediate temperatures, it was found to be possible to desorb the hydrogen from the surface SiH units, leaving a disordered silicon layer. Disilane adsorbs dissociatively on this surface and thus it is possible to grow thick silicon films under these conditions. Infrared experiments are under way on the growth of these thicker films.

Acknowledgments

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References

[1] Chabal Y J and Patel C K N 1984 *Phys. Rev. Lett.* **53** 210
[2] Chesters M A, Horn A B, Kellar E J C, Parker S F and Raval R 1989 *Mechanisms and Reactions of Organometallic Compounds with Surfaces* ed D J Cole-Hamilton and J O Williams (New York: Plenum)
[3] Davies G H and Yarwood J 1989 *Langmuir* **5** 229
[4] McGonigal M, Bermudez V M and Butler J E 1990 *J. Electron. Spectrosc. Relat. Phenom.* **54/55** 1033
[5] McCash E M, Chesters M A, Gardner P and Parker S F 1990 *Surf. Sci.* **225** 273
[6] Lu Z H, Sham T K, Norton P R and Tan K H 1991 *Appl. Phys. Lett.* **58** 161
[7] Raval R, Parker S F, Pemble M E, Hollins P, Pritchard J, and Chesters M A 1988 *Surf. Sci.* **203** 353
[8] Chesters M A, Horn A B, Ilharco L M, Ransley I A, Sakakini B H and Vickerman J C 1990 *J. Electron Spectrosc. Relat. Phenom.* **54/55** 677
[9] Chesters M A and Horn A B 1991 in preparation
[10] Chesters M A 1986 *J. Electron Spectrosc. Relat. Phenom.* **38** 123