Surface Science 209 (1989) 151–158
North-Holland, Amsterdam

THERMAL AND PHOTOCHEMICAL VAPOUR DEPOSITION OF Fe FROM $Fe(CO)_5$ ON Si(100)

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Received 24 August 1987; accepted for publication 6 October 1988

The adsorption of $Fe(CO)_5$ on Si(100) has been studied using AES and TDS techniques; pyrolytic and photochemical decomposition reactions have been examined. The adsorbate is found to undergo a dissociative, activated adsorption reaction above 300 K resulting in formation of an Fe film in which the carbon and oxygen concentrations are a few atomic percent. The sticking probability associated with the reaction is in the range 10^{-3}–10^{-4} at 500 K and the apparent activation energy is 26 ± 2 kJ mol^{-1}. UV photolysis of adsorbed $Fe(CO)_5$ is found to produce a film of similar purity. Surface-to-bulk transport of Fe is observed above 400 K. The kinetic data can be described on the basis of a model where the rate is controlled by bulk solubility levels and diffusion coefficients for Fe in Si. The situation is contrasted to that observed at high temperatures where silicide formation generates a diffusion barrier. $Fe(CO)_5$ is found to adsorb significantly more strongly on the deposited Fe film than the Si(100) substrate itself.

1. Introduction

The deposition of metal films on semiconductors through the controlled decomposition of suitable vapour phase precursor species is an important route to the metallisation of semiconductor devices [1,2]. The reaction can be driven thermally, by heating the substrate, or photochemically by UV irradiation at the solid–vapour interface [2]. In both cases the important elementary steps in the overall conversion can be limited to the adsorbed phase, depending on reaction conditions and the system under study. We have undertaken the study of such reactions and in this paper report on the $Fe(CO)_5$/Si(100) interaction.

2. Experimental

All experiments were performed in an UHV chamber equipped with LEED and AES facilities, and a 0–100 amu quadrupole mass spectrometer which was used for thermal desorption analysis. The experimental arrangement has been described elsewhere in detail [3]. The Si(100) sample (p-type, 2.4 Ω cm) was in

0039-6028/89/$03.50

the form of a thin wafer which could be heated and cooled in the temperature range 77–1500 K. The specimen was degreased and rinsed in de-ionised water prior to insertion in the vacuum chamber, and slow heating/cooling cycles to 1500 K were sufficient to produce the familiar Si(100)(2 × 1) superstructure [4] where the only contaminant present was C at a concentration of ~ 0.02 monolayers, as determined by LEED and AES. The C contamination could not be removed by heating alone and Ar^+ bombardment/annealing cycles were periodically employed to restore C concentration levels to that noted above. UV irradiation was from a 100 W low pressure Hg lamp which was focused onto the surface using quartz lenses and a sapphire viewport; the optical efficiency was such that ~ 1% of the total lamp output was incident per unit area (cm^{-2}) on the sample.

3. Results

3.1. Thermal decomposition

As we have shown previously [3] reversible molecular adsorption of $Fe(CO)_5$ on Si(100) is only significant at low pressures at temperatures below 160 K;

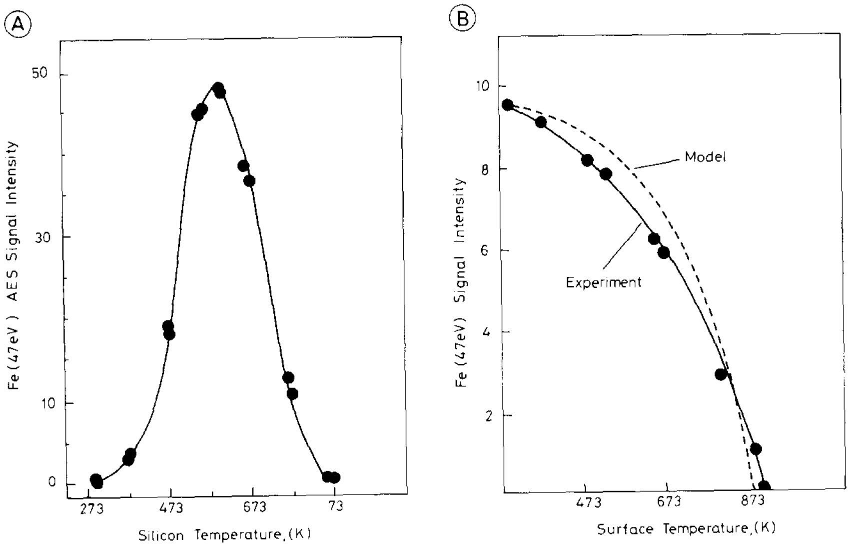

Fig. 1. (A) Plot of Fe(47 eV, $M_{2,3}VV$) AES peak-to-peak signal intensity against temperature for exposure of 10^{22} molecules of $Fe(CO)_5$ to the silicon crystal. (B) Fe(47 eV, $M_{2,3}VV$) signal intensity at 300 K against temperature at which the sample is successively annealed for 5 s, for a film of thickness 0.8 nm deposited at 300 K. Solid line: experiment; broken line: theory (see section 4).

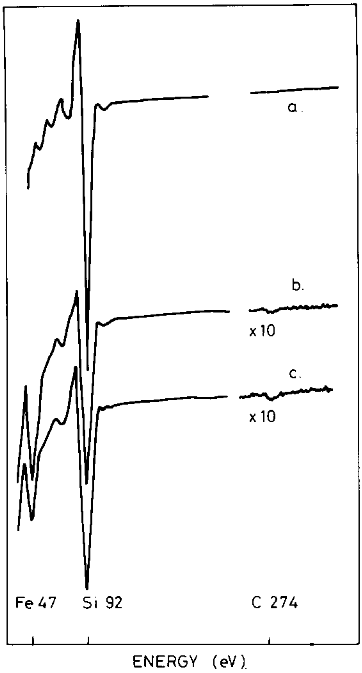

Fig. 2. (a) AES spectra of clean Si(100). (b) Film deposited thermally at 525 K. (c) Film deposited photochemically at 77 K followed by heating to 300 K.

the detection of Fe species on the surface at higher temperatures must therefore arise through the onset of decomposition. Auger analysis of the surface following exposure to 10^{22} molecules m^{-2} $Fe(CO)_5$ at differing fixed temperatures in the range 300–1000 K reveals that Fe is deposited and a plot of the Fe(47 eV, $M_{2,3}VV$) peak-to-peak Auger signal height in the differential spectrum versus deposition temperature is illustrated in fig. 1A. The increased deposition rate with temperature in the range 300–550 K is as expected if the surface decomposition reaction is activated. An insight into the origin of the fall off in the Fe Auger signal as the temperature is increased still further comes from the data in fig. 1B which displays an Fe Auger signal intensity versus temperature plot for a thin Fe film, showing the onset of bulk diffusion.

An Auger spectrum taken following exposure of the Si(100) surface to 10^{22} molecules m^{-2} $Fe(CO)_5$ at 525 K is presented in fig. 2b; it is apparent that carbon and oxygen as well as Fe is present on the surface. Using Auger sensitivity factors [5], it can be calculated that the concentration of contaminants is approximately 4% of that of the Fe, assuming that they are distributed uniformly within the Fe adlayer; in line with this, the kinetic energy of the $Fe(M_{2,3}VV)$ valence peak lies at 47 eV which is characteristic of pure Fe and the Si(92 eV) Auger peak profile does not display the change associated with formation of SiC when a heavily contaminated Fe film is deposited [3].

3.2. Photochemical deposition

$Fe(CO)_5$ was physisorbed on the Si(100) sample at 77 K which was then exposed to UV radiation. Mass spectrometric detection indicated that no Fe-containing species were evolved from the surface during this procedure but evolution of CO could be detected; a plot of the associated mass spectrometer output versus time is shown in fig. 3A. The rate of CO evolution is found to fall off rapidly in an initial phase after which time the evolution rate varies much more slowly. Auger analysis of the adlayer after prolonged UV exposure (600 s) at 77 K still showed appreciable C and O signals in the spectra. However a comparatively clean Fe film was obtained (fig. 2c) if the film was heated to 300 K prior to recording the Auger spectrum. This annealing procedure caused the desorption of CO but no Fe containing species. In contrast species containing Fe could be found to desorb if the UV irradiation time was reduced and representative desorption spectra are illustrated in fig. 3B. Unfortunately the exact nature of the desorbing $Fe(CO)_x$ species cannot be deduced because of the limited scan range of the mass spectrometer. It is nevertheless apparent that the UV light causes a significant shift in the desorption energy as witnessed by the large change in desorption temperature.

Exposure of the clean Si(100) surface to $Fe(CO)_5$ at 300 K results in negligible adsorption since the temperature is too high for formation of the molecularly adsorbed layer but too low to produce dissociation. If $Fe(CO)_5$ is exposed to the photochemically deposited Fe film at 300 K this situation is

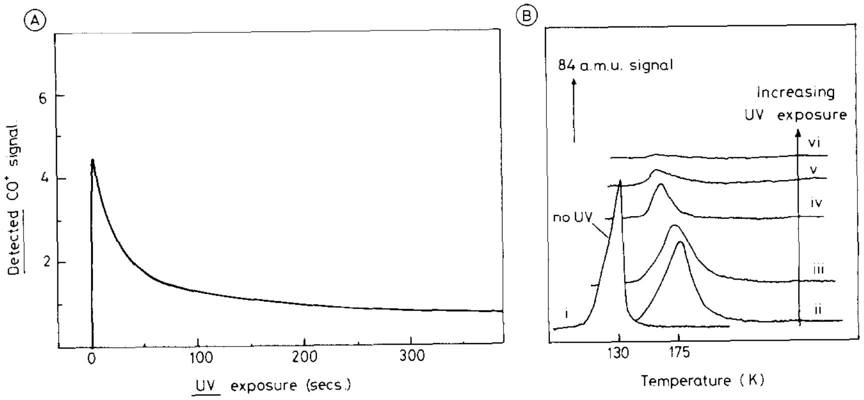

Fig. 3. (A) Plot of rate of evolution of $CO_{(g)}$ against time during UV exposure to physisorbed $Fe(CO)_5$ phase of estimated thickness 5 monolayers. (B) TDS spectra of physisorbed $Fe(CO)_5$ film exposed to UV irradiation for increasing ((i)–(vi)) times. $Fe(CO)^+$ is the detected ion.

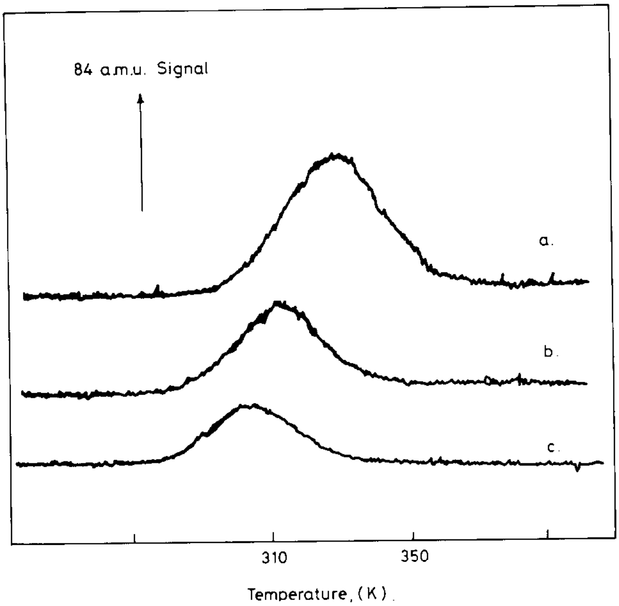

Fig. 4. TDS spectra, monitoring $Fe(CO)^+$ for $Fe(CO)_5$ adsorbed on Fe film. Gas exposures (a) 1000 L, (b) 500 L, (c) 300 L.

found to change; subsequent thermal desorption analysis results in the evolution of iron carbonyl species as shown in fig. 4.

4. Analysis and discussion

The present work shows that both the photochemical and pyrolytic decomposition of $Fe(CO)_5$ on Si(100) can be used for the deposition of Fe layers of fairly high purity, where the concentration of C and O contaminants is of the order of a few at%. Non-UHV studies (e.g. refs. [6,7]) have generally produced much higher contamination levels; thus it appears likely that such contamination results from non-optimal reaction configurations rather than arising from intrinsic reactions occurring at the $Si/Fe(CO)_5$ interface.

The thermal deposition reaction (fig. 1A) is dominated by two processes:

$$Fe(CO)_{5(g)} \rightarrow Fe_{(ads)} + 5CO_{(g)}, \quad (1)$$

$$Fe_{(ads)} \rightarrow Fe_{bulk}. \quad (2)$$

Reaction (1) is likely to involve a number of sequential elementary steps but the subsequent steps must proceed at least at the same rate as the step which results in the irreversible trapping of the molecule onto the surface since it was not possible to isolate intermediates in high concentration. Deposition dominates over diffusion at low temperatures and hence the leading edge of the plot in fig. 1A can be used to extract an activation energy for deposition. The value calculated is 26 ± 2 kJ mol^{-1}; as usual in surface dissociation reactions this is substantially lower than the Fe–CO bond strength (~ 220 kJ mol^{-1} [8]). If we assume (e.g. refs. [9]) that the original Fe Auger signal from a layer of thickness $x(I_x^{Fe})$ is given by

$$I_x^{Fe} = I_\infty^{Fe}(1 - e^{-x}/\lambda_{Fe}), \qquad (3)$$

where $\lambda_{Fe} \approx 0.6$ nm [8], then the available Auger data can be used to establish the Fe film thickness resulting from a particular gas exposure. In turn, the film thickness can be converted to absolute quantities of Fe deposited if it is assumed that the density of the film equals that of bulk Fe. Such approximations enable the sticking probability to dissociative adsorption to be calculated and it is found to be low, in the range 10^{-3}–10^{-4} at 500 K.

The diffusion process competes with deposition and has a particularly important bearing on the nature of the surface film produced; it is therefore useful to establish a realistic physical model describing surface-to-bulk transport and the data in fig. 1. Silicide formation does not take place below 700 K [10] so the loss of Fe from the surface at lower temperatures must involve a solid solution of Fe in Si. Under such circumstances Schouten et al. [11] have suggested that surface-to-bulk transport involves formation of a saturated selvedge region at the adlayer–substrate interface and rate-limiting bulk diffusion from this selvedge. The solubility of Fe in Si is low (~ 10^{22} atoms m^{-3}) in the relevant temperature range [12]. Consequently Fe in the sevedge and bulk solution will make a negligible contribution to the Fe Auger signal; the measured signal intensity will effectively arise exclusively from the Fe film itself and will decay as the quantity of Fe sorbed by the bulk rises.

In the present case, the selvedge essentially acts as a constant plane source of material for bulk diffusion and the amount of material sorbed by the bulk per unit area at time t (C^t) is given by

$$C^t = 2C_b\sqrt{Dt/\pi}, \qquad (4)$$

where D is the bulk diffusion coefficient and C_b is the bulk solubility limit [11]. Eq. (4) can be used to compute the temperature–time dependence of the Fe film thickness arising from diffusion which can then be related to Auger intensity via eq. (3). The bulk diffusion coefficient of Fe in Si is given by the equation

$$D_T = D_0 \exp(-E/RT), \qquad (5)$$

where $D_0 = 2.4 \times 10^{-6}$ m^2 s^{-1} and $E = 67$ kJ mol^{-1} [13]. By using eqs. (3)–(5), theoretical data relating to the experimental results can be computed using C_b as a variable parameter and the theory and experiment is compared in fig. 1B. The best fit is achieved with a value of $C_b = 1.3 \times 10^{23}$ atoms m^{-3} which is comparable to values of $\sim 10^{22}$ atoms m^{-3} quoted previously [12]. The conclusion is that the mass transport of Fe films on an atomic scale thickness into Si can be satisfactorily described on the basis of rate limiting bulk diffusion of Fe through the Si lattice.

It is interesting to note that this is *not* the case if comparable experiments are carried out using thicker Fe films of ~ 3 nm [10] where plateaus corresponding to distinct silicide phases are observed in Auger intensity time plots equivalent to the data in fig. 1b. The difference arises because the surface Fe concentration in the present instance drops to sub-monolayer levels before the temperature is raised to where silicide formation occurs; this is not the case for the thicker Fe films. Comparison of the present and previous data [10] also brings out the notable point that the rate of Fe dissolution at the Fe/Si interface is far more rapid than for interfaces which have been annealed to form iron silicide phases: the silicide thus serves as a diffusion barrier.

The photochemical experiments reveal that photolysis of physisorbed $Fe(CO)_5$ also provides a viable (low temperature) route for the deposition of pure Fe films. The UV photolysis of $Fe(CO)_5$ has been the subject of extensive study [14] and is believed to proceed via formation of $Fe(CO)_4$ which can then react with adjacent pentacarbonyl species forming $F_2(CO)_9$, $Fe_3(CO)_{12}$, etc. It is possible that a similar mechanism may be applicable in the present case since the large shift in desorption energy which takes place upon photolysis would be consistent with formation of (less volatile) polynuclear species. Certainly the data at least indicate that the photolytic conversion involves formation of intermediates which bond far more strongly to adjacent Fe centres. The course of the photolytic reaction was found to be insensitive to $Fe(CO)_5$ coverage from sub-monolayer up to multilayer concentrations, as deduced from the CO evolution measurements and the TDS data on intermediates (fig. 3). This implies that the underlying Si substrate plays little role in the reaction; it is also consistent with the tendency for island formation which has been previously reported for this system [3]. It is apparent from the results (fig. 4) that $Fe(CO)_5$ adsorbs significantly more strongly on Fe than on Si surfaces as witnessed by the increased desorption temperature (~ 140 K on Si [3]). Reports in the literature have described a "prenucleation effect" whereby photodeposition occurs at a significantly greater rate on the growing metal film in comparison to the "inert" starting substrate [15]. It is likely that the marked shift in adsorption energy seen here is one of the main contributing factors underlying such observations.

Acknowledgement

We gratefully acknowledge GEC Hirst Research Centre for partial financial support and Tormo Ltd. for donation of sapphire wafers.

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