THE INTERACTION OF WF6 WITH Si(100); THERMAL AND PHOTON INDUCED REACTIONS

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The thermal and UV photon-induced interaction between WF_6 and Si(100) has been examined using AES and thermal desorption mass spectrometry. At 77 K WF₆ physisorbs on the silicon surface. Above 150 K dissociative chemisorption phases are formed, which decompose in three distinct stages as the temperature is raised in the range 300–900 K to desorb silicon fluoride and produce a Si/W interface. The results suggest that WF₆ rapidly forms a thin corrosion film on Si(100) above 300 K which exerts a pronounced passivating effect as the layer begins to thicken. Rapid reaction requires Si interdiffusion into this growing film and desorption of silicon fluorides; hence the steady state reaction rate increases markedly in the temperature regime 300–400 K where the rate of these processes rises to become comparable to the WF₆ flux to the surface. Spontaneous evolution of SiF_x species is observed as a competing pathway to chemisorption and the origin of this phenomenon is discussed. Low intensity UV light from a deuterium lamp is found to have no effect on the dissociative states formed by WF₆ on Si(100). In contrast, photon irradiation is found to bring about the rapid dissociation of molecularly adsorbed WF₆, resulting in the formation of surface species which evolve SiF₄ at significantly lower temperatures than for the thermal process.

1. Introduction

Tungsten and tungsten disilicide are becoming increasingly important materials in VSLI technology for use as diffusion barriers and electrical contacts at semiconductor interfaces [1]. The characteristics of the junctions formed are superior to those based on aluminium and polysilicon. A thermally driven chemical vapour deposition reaction of the form

$$WF_6(g) + 3 \operatorname{Si}(s) \rightarrow 2 W(s) + 3 \operatorname{Si}F_4(g)$$

presents an attractive route for the deposition of the required W films on Si [2]. While lithography can be employed to achieve the necessary spatial definition, so called "direct-writing" based on non-thermal reactions driven by spatially defined ultra-violet [3], ion or electron beams [4,5] can be used to achieve the same end in a single step process. In this paper we investigate the elementary thermal, and photon-induced surface chemical reactions which underly these microscopic processes.

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2. Experimental

All experiments were performed in a stainless steel ultra-high vacuum system which has been described in detail elsewhere [6]. The apparatus is equipped with standard display-type three grid LEED optics, which were also used as an RFA analyser for AES measurements. All AES and ESD data employed a $\sim 1 \text{ mm}^2$, $1 \mu A$, 2.5 keV electron beam which was incident on the sample at a glancing angle; AES spectra were monitored in the differential mode and intensity measurements refer to peak-to-peak heights. The apparatus was also equipped with a 0-200 amu mass spectrometer, with line-of-sight to the sample, which was used for gas analysis and thermal desorption studies.

The silicon wafer (p-type, 2.4 Ω cm) of approximate dimensions 10×15 mm² was attached by tantalum clips to a liquid nitrogen cooled sapphire block. Resistive heating enabled the sample temperature to be controlled accurately in the range 77–1500 K as measured by a chromel-alumel thermocouple pressed against the rear face. The specimen was cleaned initially by slow heating cycles to 1500 K after which treatment the surface displayed the familiar (2 × 1) LEED pattern and carbon remained the only impurity present at an estimated concentration of ~ 0.01 monolayers. Heating to high temperatures was also initially useful at cleaning the sample following adsorption experiments involving WF₆. However this treatment (which brings about surface-to-bulk diffusion of W) gradually became less effective as the bulk concentration of W increased. It was therefore necessary to change samples frequently as the experiments progressed.

Exposure to UV employed a deuterium lamp which was focused onto the sample through quartz lenses and a sapphire viewport. WF₆ was dosed on to the surface through a capillary dosing tube which developed a pressure enhancement of $\sim 10^3$ in the region of the Si crystal.

3. Results

3.1. Thermal reaction

 WF_6 was exposed to the sample at differing temperatures and the surface was then examined using TDS and AES to elucidate the nature of the adsorbed layers formed.

Thermal desorption analysis of the phase formed at 77 K revealed a single peak at 130 K in the W⁺ (185 amu) ion spectra for exposures in the range 0-30 L. Spectra monitoring F⁺ (19 amu) exhibited identical profiles and AES analysis following desorption demonstrated only very low concentrations of W and F remained on the surface. This indicates that reactant stoichiometry is largely maintained during an adsorption-desorption cycle at low temperatures



Fig. 1. (A) Thermal desorption spectra in the range 300-800 K following increasing exposures (0.1-1500 L) of WF₆ to Si at 300 K. Detected ion: SiF. (B) Similar to (A) for exposures of 0.1-60 L in the temperature range 750-950 K.

with the W⁺ and F⁺ ion signals resulting from the ion source fragmentation of WF₆. In line with this, the thermal desorption characteristics showed little change as the surface coverage rose from sub-monolayer to multilayer coverages (as judged by the appearance of interference fringes). The heat of adsorption calculated using the Redhead formula with $\nu = 10^{13} \text{ s}^{-1}$ is 31 kJ mol⁻¹ is in agreement with the heat of vaporisation of WF₆ (33.8 kJ mol⁻¹). This situation suggests that the low temperature interaction of WF₆ with Si is essentially limited to physical adsorption. This situation changes dramatically if the exposure temperature is increased to 300 K. No thermal desorption of W containing species can be detected following such exposures but signals corresponding to F⁺ and SiF_x (x = 0-4) species are observed. Thermal desorption spectra monitoring SiF⁺ ion currents are presented in fig. 1. Three desorption states denoted α , β , γ are displayed and the desorption yields of



Fig. 2. Uptake curves derived from measured SiF⁺ ion currents for the α , β , γ states displayed in fig. 1.



Fig. 3A. Time dependence of the (largely SiF₄) derived SiF₃⁺ ion current during exposure of the Si crystal to -10^{-6} mbar WF₆ at (upper trace) 725 K and (lower trace) 295 K.



Fig. 3B. Plot of the rate of steady state evolution of SiF₄ against surface temperature.

the separate states are plotted out as a function of coverage in fig. 2. The γ and β states populate simultaneously and saturate at high exposures in contrast to the α state which grows on a slower time scale. Although no desorption of W species could be detected, AES indicated that W was present in the interfaces formed in these experiments and the uptake kinetics were similar to that illustrated for the γ and β states in fig. 2. Comparison of the relative ion currents corresponding to differing SiF_x (x = 0-4) species with tabulated cracking pattern data [7] suggested that the desorption products from the α and β state were largely SiF₄ species; a similar analysis for the γ state indicates that SiF₂ also becomes an important desorption product, along with some SiF₃ and SiF species. Thermal desorption studies were performed for differing adsorption temperatures in the range 300-900 K; the spectra were essentially similar to those recorded at 300 K, with the expected difference that no desorption below the exposure temperature was observed. While the data presented above refer to the formation of adsorbed states, gas phase analysis during dosing revealed spontaneous evolution of SiF_x species into the gas phase takes place. Below 600 K, SiF₄ is the predominant species evolved while SiF_x species also become principle products at higher temperatures. Plots of the rate of evolution of SiF_4 versus exposure time to WF_6 at two



Fig. 4. (A) Plot of the W(169 eV) peak-to-peak height following 1500 L WF₆ exposure at differing temperatures. (B) Plot of the W(169 eV) (B) and Si(92 eV) (O) Auger peak heights following flashing of a 3 nm W film on Si(100) to successively increasing temperatures.

differing temperatures are shown in fig. 3A. The evolution rate has a maximum at the initiation of the exposure (within the ~ 1 s time resolution available), and decays to an almost constant "steady-state" value. The temperature dependence of this steady state rate is shown in fig. 3B. Below 300 K the evolution rate remains small but finite while the rate of SiF₄ evolution increases rapidly above 350 K.

The surface was exposed to 1500 L WF₆ to saturate the surface with W at differing temperatures and the surface W concentration was analysed by AES. The results are illustrated graphically in fig. 4. The amount of W deposited increases rapidly in the range 300-500 K and then falls off as the temperature is raised. In order to investigate this in more detail, the Si and W Auger intensities from a Si surface on which a ~ 30 Å W film was deposited by electron beam [4] was measured as the surface was heated in vacuo; the results are presented in fig. 4B. No desorption of W containing species occurred in



Fig. 5. Thermal desorption traces of W⁺ (185 amu), SiF₂⁺ (66 amu) and SiF₃⁺ (85 amu) species following (a) zero (b) 15 min (c) 90 min UV radiation of a 0.1 μ m physisorbed adlayer of WF₆.

this experiment and so the loss of W observed must result from surface-to-bulk transport.

3.2. Effects of UV radiation

It is apparent from the results outlined above that surfaces of differing character can be prepared depending on the crystal temperature during WF₆ adsorption. Experiments were therefore performed to examine how these interfaces behaved when exposed to low intensity UV light. No UV-induced effects could be observed on surfaces which had been dosed with WF₆ at temperatures of 300 K or above so as to display variable α , β , γ desorption state concentrations. However UV-induced reactions were observed for the physisorbed WF₆ phase.

In one set of experiments, physisorbed WF_6 layers of varying coverage were temperature programmed after exposure to UV for differing times and the results are presented in fig. 5. In the absence of UV light the data display a single W⁺ peak arising from desorption of physisorbed WF₆ at 130 K. As the UV exposure increases, desorption shifts to higher temperatures and silicon fluorides, mainly SiF₄, become a principal desorption product. These observations were not sensitive to coverage in the multilayer regime but the situation



Fig. 6. Variation of SiF_4 derived SiF^+ ion current with time during switching of the deuterium lamp.

changed at submonolayer WF_6 concentrations; although UV photolysis reduced the amount of WF_6 desorbing, no SiF_x species could be detected in the thermal desorption scan. Clearly UV light is capable of driving a reaction resulting in the formation of SiF_x at the expense of WF_6 species. Accordingly, after desorption of the volatile species present, W could be detected on the surface by AES and pure W films of a thickness of the order of the Auger sampling depth could be straightforwardly prepared at high WF_6 precoverages. Gas phase analysis also indicated that SiF_x was evolved directly into the gas phase during photolysis. Typical experimental data is shown in fig. 6. The rapid modulation of detected SiF_x species with chopping of the light beam confirms the occurrence of photon stimulated desorption.

4. Discussion

4.1. Thermal reaction

It is apparent from the results that WF_6 adsorbs in a molecular form on Si(100) at 77 K into an essentially physisorbed state which largely undergoes reversible desorption as the temperature is raised. No chemisorption states can be populated with appreciable sticking proability at low temperatures suggesting that the Si-WF₆ molecule bond is limited to physical interactions. In contrast dissociation reactions clearly take place at higher temperatures confirming that dissociative adsorption is an activated process. Three adsorbed states of bound fluorine are resolved in the thermal desorption experiments. The uptake curves for the observed β and γ forms are essentially associated with a two-dimensional phase whereas the α state arises from the onset of bulk corrosion. The β and γ states populate simultaneously suggesting that they are likely to arise from the sequential degradation of a common precursor on the surface rather than from the initial population of two differing forms. Roop et al. [8] have studied thermal desorption from (W-free) fluorinated Si surfaces and observed two states with desorption temperatures and products rather similar to the β and γ forms seen here; they attribute the first desorption peak to the transformation of a fluorine-rich SiF, phase into one with a lower average F: Si coordination number and the second peak to the decomposition of this phase. Since the Auger data (fig. 4B) indicate that surface-to-bulk W transport occurs below 600 K, the similarity between the two sets of results is understandable.

To a large extent, the observations at 300 K are consistent with a WF₆/Si interaction exclusively giving rise to the rapid formation of a 2D W, Si, F mixed selvedge, with uptake slowing dramatically when this phase covers the surface; and further adsorption vests on film thickening through the gradual population of the α state. This is a classic picture for the growth of corrosion

films. However the situation changes markedly if adsorption is carried out at higher temperatures. Although the desorption yields from the relevant α , β , γ adsorption states which are stable at the particular dosing temperature remain constant, the W "saturation" Auger signal rises and falls in a disconnected way as the adsorption temperature is varied. Spontaneous evolution of SiF_x species occurs at a rapid rate even at high gas exposures where the W Auger signal saturates. This behaviour arises because interdiffusion between the selvedge region and the underlying substrate begins to play an important role. The low pressure WF₆/Si reaction is probably best viewed as follows:

(a) $T \leq 150$ K: Dissociative adsorption of WF₆ is rate limiting, and the overall deposition rate is negligible since the activation barrier for the process cannot be surmounted.

(b) $150 \le T \le 350$ K: Dissociative adsorption becomes appreciable, resulting in the rapid formation of a W, Si, F selvedge region (β and γ states populated). Adsorption slows (α state uptake) as the layer thickens and becomes depleted of Si; slow interdiffusion required for layer thickening is rate limiting.

(c) $350 \le T \le 550$ K: Rapid saturation of the β and γ states takes place. The surface is now in the temperature range where the α state decomposition through interdiffusion and SiF_x desorption begins to occur on the same time scale as dissociative WF₆ adsorption. Hence the "steady-state" rate of SiF₄ evolution rises sharply since the passivating film is no longer stable (fig. 3B) and the amount of W deposited increases.

(d) $T \leq 500$ K: Dissociative adsorption is rapid. All bound forms of fluorine become unstable on the surface and W diffusion into the bulk is rapid. The steady-state rate of SiF_x evolution becomes rate limited by mass transport to the surface. The W concentration in the surface layers remains low because of rapid transport into the bulk.

This model satisfactorily accounts for the Auger and thermal desorption analysis of the surface after WF₆ exposure, over the temperature range investigated, and the temperature dependence of the SiF_x(g) evolution rate. It also explains why deposition below 500 K evolves SiF₄(g) since this is associated with decomposition of the α state; above 500 K the more weakly fluorinated surface becomes stable and thus the products evolved begin to match the β and γ states. However disagreement with the model and experimental data exists in one respect. Spontaneous evolution of SiF₄(g) occurs at temperatures below the range where α , β , γ phase evolution takes place; spontaneous evolution begins immediately when WF₆ exposure commences and no incubation period is observed while chemisorption states populate. We believe the explanation for this arises from the fact that dissociative WF₆ adsorption momentarily results in a high local concentration of fluorine in the region of the dissociating molecule. This high concentration then spontaneously decays either by evolution of an SiF_x molecule into the gas phase, or by diffusion resulting in a drop in the F: Si concentration ratio to a value when the phase is stable on the surface at the particular temperature under investigation.

4.2. Photochemical deposition

The results presented here show that the dissociative states formed by WF_6 on Si(100) are insensitive to the low intensity visible/UV radiation emitted by the deuterium lamp. Houle [9,10] has observed stimulated desorption of SiF_x species from fluorinated silicon surfaces using 508 nm band gap radiation from an Ar laser; however the desorption yields exhibited a quadratic or quantic dependence on radiation power and thus the power density used in this work is insufficient to observe such effects. It also follows that all the photolytic reactions observed for molecularly adsorbed WF₆ cannot have the same origins as those observed by Houle, even through some of the observations (e.g. photon-induced desorption of SiF_x) are qualitatively similar.

The surface photochemical deposition of W differs from the thermal reaction in a number of important respects. Most obviously UV light is capable of overcoming the thermal activation barrier for WF₆ dissociation. The mechanism by which this occurs is as yet unknown. WF₆ absorbs strongly in the near UV region whilst electronic excitations in the substrate and reactions driven by emitted photoelectrons must also be considered [11]. SiF_4 represents a principal thermal desorption product from photolysed WF₆ multilayers showing that photolysis stimulates the reaction between WF_6 and Si, rather than simply leading to photon stimulated desorption of fluorine. SiF₄ is evolved spontaneously into the gas phase during photolysis, even at 77 K. Surprisingly, this occurs for thick WF_6 (interference fringes visible) coverages where diffusion of SiF_4 through the frozen WF₆ adlayer would not be expected. Possibly this arises because of a WF₆ coverage inhomogeneity across our sample. The SiF₄ which is observed to desorb in the thermal desorption experiments (fig. 5) could then arise from the formation of SiF_x species which are trapped on the surface by the overlying WF_6 film. Some support for this comes from the observation that no thermal desorption of SiF_x species is detected during thermal desorption of thin WF₆ phases and that thermal desorption of SiF_x takes place at the temperature where the WF₆ layer is stripped off. An important point to note is the fact that SiF_x species are evolved during photolysis and subsequent thermal desorption of photolysed phases at significantly lower temperatures than in the purely thermal WF_6/Si interaction. This is likely to have two origins. Firstly, the diffusion of charge carriers, created by band gap radiation, to the surface tends to enhance the rate of SiF bond formation over other processes leading to formation of more strongly fluorinated (and hence more volatile) phases [9,10]. Secondly the photochemical reaction can be carried out at low temperatures where Si/F

interdiffusion presumably occurs to a lesser extent, this also permitting formation of more strongly fluorinated, volatile surface species.

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