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Influence of carbon on the electron stimulated desorption from titanium silicide surfaces

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Abstract

The influence of carbon on the electron stimulated desorption from titanium silicide thin film surfaces has been studied by means of electron-stimulated-desorption (ESD) and Auger electron spectroscopy. The superficial carbon was due to exposure to air. The main ions ejected were O^+ , H^+ , and minor amounts of OH^+ . Ion emission intensity versus incident electron energy showed threshold energies corresponding to the Ti 3p and Si 2p core levels, in agreement with the Knotek–Feibelman model. Intensity and shape of the H^+ ion yield curves depended markedly on the amount of carbon contamination remaining after Ar^+ ion cleaning. Ion yield measurements on the low carbon concentration surfaces showed both thresholds due to excitation of the Ti 3p and Si 2p core levels. On the contrary, for high surface carbon concentrations, ions are only ejected by excitation of the Ti 3p levels. The differences between the ESD yield for H^+ and O^+ after exposure to air have been studied.

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1. Introduction

The resonant electron discharge in vacuum in high-power RF electromagnetic fields in cavities or wave guides is a phenomenon known as the multipactor effect. In order to reduce the feedback of this resonant electron discharge, titanium silicide, a refractory metalloid, appears to be a promising material for anti-multipactor coatings, due to its low secondary electron emission yield. Silicides such as TiSi₂ have a reasonably low resistivity ($\leq 50 \ \mu\Omega \ cm$) [1], although they are mainly composed of a non-metallic element. For instance, the

adsorption/desorption kinetics of SiH₄ on polycrystalline TiSi₂ behaves as in typical metals [2]. Surface application of metal silicides to improve electrical properties of field-emitter arrays has also been studied [3].

For anti-multipactor applications, the behavior of a coating under air exposure and its desorption response upon electron and ion bombardment is as important as a low secondary emission yield. After air exposure, before operation, the coatings are usually subjected to a *conditioning* treatment, i.e., the RF field is increased until the multipactor threshold is reached momentarily. Consequently, the coating is bombarded with electrons and ions and some desorption of ions is achieved resulting in the recovery of anti-multipactor properties.

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Electron multipactor discharge can produce enough gas desorption as local conditions for plasma ion discharge (Corona) are reached. This evolution of the multipactor discharge into a more destructive Corona discharge is one of the main problems of the multipactor effect in technological applications. Therefore, the study of a potential antimultipactor coating should include the surface desorption of ions during electron bombardment [4]. The main objective of this work was, therefore, to study the influence of exposure to air and subsequent Ar^+ ion etching on the desorption of O⁺, OH^+ and H⁺ ions from the TiSi₂ surface.

2. Experimental

Thin titanium silicide films were deposited on Si(100) p type wafers by magnetron cosputtering from Ti and Si targets. The samples were subjected to an annealing treatment at 900 K. Rutherford backscattering analysis of the titanium silicide using standard experimental conditions: 2 MeV He⁺ ions detected at 165°, indicated a bulk composition of TiSi₂. After exposure to air, the samples showed the natural carbon surface contamination. Ar⁺ ion bombardment with variable ion flux permitted a surface composition to be obtained with gradual carbon concentration, i.e., with a smooth lateral gradient. Thus, it was possible to analyse in situ several surface regions of the sample exposed to different ion doses (fluences). The estimated dose range was $1-10 \times 10^{16}$ ions/cm² with energy of 500 eV at 60° incidence angle. No implanted Ar was detected on the sample.

To perform surface analysis, the sample is moved to an ultrahigh vacuum system incorporating Auger electron spectroscopy (AES) and electron stimulated desorption (ESD) mass spectrometry techniques. Quantitative AES was used to obtain the compositional analysis of the sample surface. Normal emission was detected using a double pass cylindrical mirror analyser. The kinetic energy of the incident electron beam was 3 keV with a current of 100 nA. ESD experiments were performed with the axis of the electron gun at 45° to the normal of the sample. Energy of the incident electron could be varied from 5 to 100 eV and the current was always kept at 100 nA. Positively charged products of electron-stimulated desorption were recorded using a quadrupole mass spectrometer, Hiden, Analytical LTD, UK. The QMS subtended a solid angle of 10° from the normal to the surface to detect desorbed ions. The electron gun was fixed at 45° polar angle of incidence relative to the sample normal. The ions observed to desorb were O⁺, H⁺, and minor amounts of OH⁺. All experiments were performed at a base pressure of 2×10^{-10} Torr. Measurements were performed with the sample at room temperature.

3. Results and discussion

Fig. 1 curve (a) shows the derivative AES survey spectrum obtained for the titanium silicide surface after being exposed to air. The presence of Ti, Si, C and O can be observed. The spectrum exhibits the characteristic Ti LMM, Ti LMV, Si



Fig. 1. AES spectra of the $TiSi_2$ at sample positions with decreasing carbon concentrations: 60%, 30%, 25%, 20%, 15%, 10%, and 1% corresponding to spectra (a)–(g), respectively.

KLL, C KLL and O KLL peaks, marked in the figure. The spectra (b)-(g) of Fig. 1 show the changes in the surface composition that resulted from the above described cleaning process by Ar⁺ ion bombardment. For comparison purposes, the spectra were normalized to the oxygen signal. As expected, a gradual increase in titanium and silicon signals is observed. For instance, in spectrum (g) the carbon signal has nearly disappeared, although the oxygen is still present on the surface. The composition of the different regions of the sample was determined using the relative peak-to-peak heights of the signals and the corresponding sensitivity factor for the primary energy beam, $E_p = 3$ keV [5]. Thus, the initial carbon concentration of the surface exposed to air was estimated in 60 atomic per cent in the depth probed by AES (1 nm). The carbon concentrations corresponding to spectra (b)-(g) of Fig. 1 were 30%, 25%, 20%, 15%, 10%, and 1%, respectively.

In order to characterize the initial excitation, and in consequence, the local bond of the adsorbates that produces the desorbing ion, we have measured the yield of the detected H^+ , O^+ , and OH⁺ ions as a function of the incident electron energy. Fig. 2(a)–(c) shows the total H^+ , O^+ , and OH⁺ ion yields for titanium silicide surfaces with approximately 1%, 10%, and 30% carbon concentration, respectively. It is observed that all ESD curves present a threshold at 39 eV. However, the shape of the ESD curves depended strongly on the surface carbon concentration. For the sample surface with low carbon concentration, Fig. 2(a), the ESD curves of H⁺ showed a general monotonous increase with the electron energy and a broad peak located at about 150 eV. However, the ion yield at high electron energies decreases as carbon concentration increases ((b) and (c)). This decrease was accompanied by the appearance of a second peak at high energies, at about 320 eV (b). Finally, for the surface region rich in carbon, an enhancement of the peak located at low electron energies, 150 eV, was observed. Therefore, the carbon-contaminated surface seems to desorb less hydrogen for high incident electron energies and more for low energies than the clean surface. A similar behaviour was observed for the OH⁺ ions. This interesting behaviour can be understood in



Fig. 2. ESD yields of H^+ , O^+ , and OH^+ ions as a function of the incident electron energy, from titanium silicide surfaces: (a) with low carbon, 1%, (b) with medium carbon, 10%, and (c) with high carbon concentration, 30%.

terms of the hydrogen chemisorption sites present prior to desorption.

With the aim to identify the different contributions in the ESD curves, the H⁺ ion yield curves (b) and (c) of Fig. 2, corresponding to surfaces with intermediate and high carbon concentration, respectively, have been subtracted after normalisation. We normalized the yield curves so that their difference, always positive, was minimal in the first 90 eV. We selected this value because desorption from Ti atoms is the only contribution expected below this energy, i.e., we intended to normalize to this desorption contribution and, in this way, suppress it in the difference. Fig. 3 shows this difference curve which resembles an ESD curve with a threshold at approximately 100 eV, that corresponds to the Si2p core level, and a broad peak at around 320 eV. This result allows us to explain the different shapes of the ESD curves of Fig. 2(a)-(c) as the overlapping of the signals corresponding to desorption from titanium and



Fig. 3. Difference between (b) and (c) curves of Fig. 1 after normalization of the $\rm H^+$ ions yields.

silicon atoms. Thus, the ESD curve of Fig. 2(c), corresponding to a high carbon concentration, is dominated by desorption from titanium atoms. This interpretation is also supported by the fact that higher H^+ ion desorption from titanium atoms correlates well with higher Ti composition of the surface as determined by quantitative AES. The Ti:Si atomic ratio is equal to 1.1 and 0.6 for the surfaces with high (Fig. 2(c)) and low carbon concentrations (Fig. 2(a)), respectively.

These results can be understood in terms of the core hole Auger decay mechanism proposed by Knotek and Feibelman [6] to explain electron stimulated desorption. They proposed an interatomic Auger decay as a possible mechanism for desorption. The desorption begin by the formation of a core hole in the metal atom. There is a certain probability that a valence electron from the ligand fills the metal core hole in an interatomic Auger process. As a part of this process, one valence electron of the ligand is released. The ligand atom, initially negatively charged change to positive and is repelled from the surface. In this frame, no threshold is observed at low energies corresponding to excitation of the valence band electrons, <25 eV [7,8]. In all ESD curves, the first threshold found, at approximately 39 eV, corresponds to Ti core levels. It is deduced that the H⁺ ion yield for the surfaces with high carbon concentration is mainly related to concomitant hydrogen chemisorbed on titanium. For these surfaces, only the maximum at 150 eV was observed. In contrast, ESD curves for low carbon concentration surfaces also show the maximum around 320 eV that has been assigned to hydrogen absorbed on silicon

atoms, which were located in the subsurface region before Ar⁺ ion bombardment [9]. Secondary electrons play an important function in stimulated desorption. Desorption can also be produced by secondary electron coming from the bulk to the surface. These secondary electrons are generated at different depths by the primary electrons. However, it is certainly one of the less understood subjects in desorption induced by electronic transitions. The contribution of secondary electrons is expected at energies far above the threshold [10– 12]. Maximum secondary yields are usually in the 200–800 eV range of the primary electron energy.

Fig. 4(a) and (b) show the intensity ratio of the H⁺ ion yield curve to that of O⁺, $I_{\rm H}/I_{\rm O}$, corresponding to low (Fig. 1(a)) and high carbon content surfaces (Fig. 1(c)), respectively. For the surface with low carbon contents, the relative $I_{\rm H}/$ $I_{\rm O}$ curve decays sharply to a nearly constant value. In other words, more H⁺ ions are generated at lower incident energies relative to O⁺ ions. The H⁺ desorption probability has been found to depend on the bonding character of the orbitals where holes are created and on the effective hole-hole Coulomb repulsion [13]. A different result was obtained for the surface regions with carbon. For higher carbon concentration, the H^+ and O^+ ion yield curves are similar in shape, so that the $I_{\rm H}/I_{\rm O}$ ratio was roughly constant.



Fig. 4. Relative intensity of H⁺ respect to O⁺, $I_{\rm H}/I_{\rm O}$, as a function of the incident electron energy at different regions of the TiSi₂ surface: (a) with low carbon, and (b) with high carbon concentration.

Therefore, it seems that the surface carbon concentration could play a significant role in stimulated ion desorption from titanium silicide. The adsorbed carbon could affect bonding in the titanium silicide surface. The competition between the electronic state and the local atomic coordination that determines the ion desorption behaviour was proposed for TiO_2 [14]. The effect of the adsorbed carbon on the ESD curves could be explained in terms of higher coordination numbers for the clean silicide surface. If hydrogen is chemisorbed with a high coordination number, this can result in a rapid neutralization from the neighbouring atoms following ion formation.

4. Conclusions

Hydrogen and oxygen desorption from titanium silicide exposed to air and subjected to Ar^+ ion bombardment, has been investigated by means of electron stimulated desorption and Auger electron spectroscopy. There were noticeable differences in the shape and intensity of the H⁺ and O⁺ ion yield curves depending on the different amounts of carbon contamination on the titanium silicide surfaces.

The H^+ ion yield curve of the silicide rich in carbon shows a threshold near 39 eV, which corresponds to the binding energy of the Ti 3p level. However, for the surfaces with low carbon concentration, the H^+ curve has, besides the threshold at the Ti 3p ionisation potential, a higher one at 100 eV assigned to the Si 2p ionisation potential. These excitation processes suggest that the Knotek–Feibelman mechanism is operative.

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