

Short communication

Thermal stability of ultrathin titanium films on a Pt(111) substrate

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Abstract

We report annealing studies using He⁺-ion scattering spectroscopy (He⁺-ISS) and X-ray photoelectron spectroscopy (XPS) to evaluate the thermal stability of ultrathin Ti films deposited on a Pt(111) single-crystal surface at 300 K. These results establish that strong Pt–Ti intermetallic bonding provides sufficient driving force for thermal interdiffusion of Ti and Pt at a (111)-oriented interface at 700 K (427 °C), even in the absence of oxygen and a minimal influence of grain boundaries. Identification of this critical temperature provides additional fundamental information for Ti/Pt bilayer film processing considerations. This data was obtained by using He⁺-ISS to monitor the concentration of Ti in the topmost surface layer as a function of temperature. In these studies, we define 1 dose unit (DU) to be the amount of deposited Ti that is required to eliminate the Pt signal in He⁺-ISS. This amount should be close to that required to produce a one-monolayer Ti film, but it could exceed one monolayer of Ti if alloying or clustering occurs on the substrate at 300 K under these deposition conditions. For Ti films less than 1 DU, heating to 700 K slightly decreased the Ti surface concentration. Higher annealing temperatures of up to 950 K caused extensive loss of surface Ti, and this is attributed to Ti diffusion into the Pt crystal sub-surface region. For a 1-DU Ti film, temperatures of 750–800 K were required to cause sufficient interdiffusion so that Pt atoms were detected in the topmost layer, strongly suggesting that the 1-DU Ti film was more thermally stable than those of lower Ti coverage. Thicker Ti films of greater than 1 DU required temperatures of 800–1050 K before any change was detected in the Ti surface concentration as probed by the He⁺-ISS signal intensity. After annealing to temperatures higher than 1000 K, XPS revealed a chemical shift for the Ti (2p) peaks of 1.5 eV to higher binding energy, indicating formation of a Ti/Pt alloy. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Growth of ultrathin metal films on Pt has been studied in a number of systems, for example, Cr/Pt [1,2], Co/Pt [3–6], Ni/Pt [7–9], Ag/Pt [10–12], Sn/Pt [13–15] and Si/Pt [16,17]. These systems are of interest because of their unique catalytic, electronic and magnetic properties. Interest in Ti/Pt bilayer films has increased recently because of their use in thermal and flow sensors [18–21] and in high-permittivity metal oxide capacitors for IC memories [22–24]. Despite the importance of these applications, very little basic information is available for highly controlled, well-defined Ti films on Pt.

Processing constraints in IC and sensor fabrication technology have led to the use of Ti/Pt bilayer electrodes [18,22,25]. Platinum is an excellent electrode material because it is chemically stable under high-temperature oxidizing conditions and has a high thermal coefficient of resistance (TCR). Unfortunately, Pt does not adhere well to SiO₂ or SiN_x substrates, and therefore, a thin Ti or Cr layer is deposited first to improve adhesion.

Lead zirconium titanate (PZT) and barium strontium titanate (Ba,Sr)TiO₃ (BST) have potential for use in non-volatile random access memories (NVRAMs) [26,27] or dynamic random access memories (DRAMs) [24,28] because of their remnant polarization [28]. The design structure of these devices requires the “bottom” Ti/Pt electrode to be fabricated first, directly on SiO₂. The ferroelectric thin film is then deposited by sputtering, sol gel, or chemical vapor deposition, and undergoes specific thermal treatments

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that vary in time and temperature, and can directly affect the stability of the underlying metal layers. It has been suggested that during deposition of these films at high temperature, titanium can migrate to the Pt surface through grain boundaries [22,23,25,29]. Titanium at the surface may then become oxidized, which can lead to degradation of device performance.

Thin Ti/Pt films on SiN_x/Si substrates have been investigated for thermal and flow sensor applications [18]. For these sensors, suspended-membrane Pt microheaters are fabricated on a Si wafer. Following metal deposition, substrate material directly below the heater is etched away using KOH. It is critical at this step that the deposited Pt thin film has good adhesion to the SiN_x/Si substrate to prevent peeling in the KOH solution, and that it retains its high TCR for sensor sensitivity. Here again, films of Ti or Cr are used as adhesion promoters to suppress peeling of the Pt electrode [19–21,30]. However, it has been found that post-process annealing still leads to peeling of the Pt film [22,25,31]. Therefore, the thermal stability of Ti/Pt films is very important.

Here, we present results showing fundamental aspects of the thermal stability of Ti/Pt bilayer film interfaces by probing Ti films deposited on a Pt(111) single-crystal substrate under UHV conditions using a highly surface sensitive technique (He⁺-ion scattering spectroscopy [He⁺-ISS]) to monitor the surface concentration of Ti as a function of temperature. We found that Ti interdiffuses with Pt at a temperature of 700 K, and Pt atoms appear at the surface by 800 K even for several-layer-thick Ti films. To our knowledge, there are no previous reports that evaluate the thermal stability of ultrathin Ti films deposited on a Pt(111) single-crystal surface.

2. Experimental

All experiments were performed in a multi-technique ultrahigh vacuum (UHV) chamber that is described in detail elsewhere [32]. The chamber was equipped with a Colutron ion gun that provided a collimated, monoenergetic ion source for He⁺-ISS, a dual-anode Al/Mg Kα X-ray source for X-ray photoelectron spectroscopy (XPS), an electron gun for AES, a Perkin-Elmer Model 10-360 spherical capacitor analyzer (SCA) with a multichannel detector, and reverse-view LEED optics (PRI). An electron-beam heated, Ti evaporator (Ti rods, ESPI, 6N purity) was used to deposit the Ti films. The sample was heated by electron bombardment from a filament positioned directly behind the sample. The temperature was monitored using a type-K thermocouple spot-welded directly to the side of the crystal.

A Pt(111) single crystal (Atomergic, 5N purity) was used for all experiments and was cleaned using standard procedures consisting of cycles of 500-eV Ar⁺-ion sputtering, followed by annealing in a background of 2×10^{-7} torr O₂ at 1000 K, with a final annealing in UHV at 1200 K. The condition of the sample was monitored by AES and LEED,

and cleaning was repeated until no contamination of the surface could be detected. The base pressure in the chamber was 4×10^{-10} Torr. All Ti films were deposited on the Pt substrate at 300 K and annealing experiments were performed immediately to minimize Ti oxidation by residual gases in the chamber.

The Al-Kα X-ray source in XPS was operated at 300 W (15 kV) with an SCA pass energy of 23.5 eV. He⁺-ISS measurements were made using an incident He⁺-ion-beam energy (E_0) of 1.0 keV. The SCA was operated at a pass energy of 1127.1 eV, and a complete energy scan of the scattered ion energy (E_1) could be acquired every 60 s. The angle between the SCA and ion source was fixed at 36° to give a scattering angle of 144°. Conventionally in ISS, the polar angle is defined with respect to the crystal surface plane, with $\Psi = 90^\circ$ corresponding to incident ions perpendicular to the surface. Energy scans were obtained for $E_1/E_0 = 0.4$ – 0.9 , which fully covers the scattering peaks from both Pt and Ti. The Pt and Ti scattering signal intensity was determined from integration of the single-scattering peaks after background subtraction.

3. Results and discussion

Ion scattering spectroscopy using rare gas ions is extremely surface sensitive and provides composition information on the outmost atomic layer only [33]. In He⁺-ISS, with a scattering angle of 144°, 1.0-keV incident He⁺-ions gave a large peak separation for ion scattering from Ti ($E_1/E_0 = 0.68$) and Pt ($E_1/E_0 = 0.89$) atoms at the surface.

A Ti deposition experiment was performed using He⁺-ISS to determine aspects of the Ti film growth as a function of Ti deposition. Fig. 1 shows He⁺-ISS data for increasing amounts of Ti deposited on Pt(111) at 300 K. Ti deposition lead to an increase in the Ti scattering signal and a decrease in the Pt scattering signal. The Pt peak intensity decreased rapidly with exposure time, and this was negligible by 270 s. We have assigned this Ti deposition time to 1 dose unit (DU) of Ti. Thus, we defined 1 DU to be the amount of deposited Ti that is required to eliminate the Pt signal in He⁺-ISS. This amount should be close to that required to produce a one-monolayer Ti film, but it could exceed one monolayer of Ti if alloying or clustering occurs on the substrate at 300 K under these deposition conditions.

The surface Ti concentration was calculated using the following equation:

$$\text{Ti surface concentration} = \frac{I_{\text{Ti}}/I_{\text{Ti}}^\infty}{I_{\text{Ti}}/I_{\text{Ti}}^\infty + I_{\text{Pt}}/I_{\text{Pt}}^\infty} \quad (1)$$

where I_{Ti} and I_{Pt} are the He⁺-ISS intensities (scattering yields measured as integrated peak areas) obtained for a given surface and I_{Ti}^∞ and I_{Pt}^∞ are intensities measured for a thick, pure-Ti film and the clean-Pt(111) surface, respectively. Concentrations determined by using Eq. (1) are

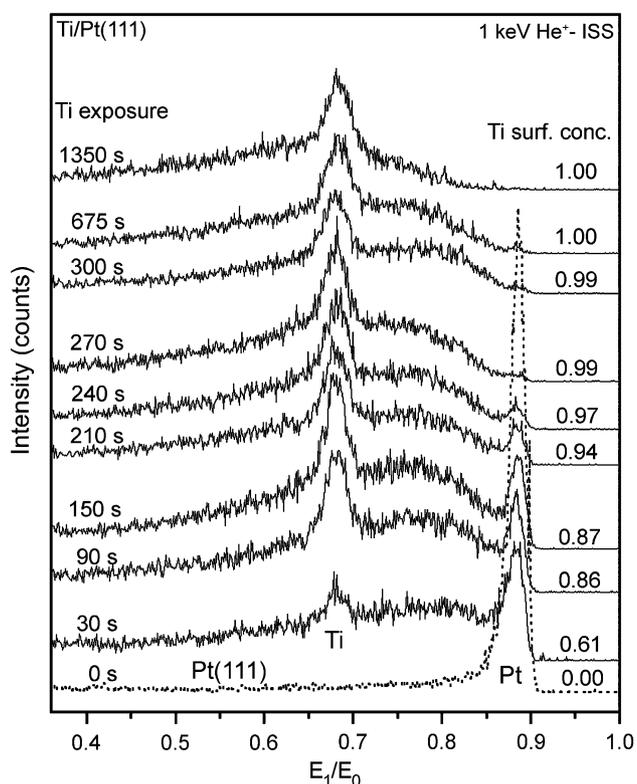


Fig. 1. He⁺-ISS spectra for a series of increasing amounts of Ti deposited on Pt(111) at 300 K. The Ti concentration in the topmost surface layer as determined by He⁺-ISS was calculated by using Eq. (1).

plotted versus Ti exposure time in Fig. 2. It is clear in the figure that the Pt(111) surface is completely covered by an exposure time of 270 s.

In Fig. 3, Ti surface concentration is plotted versus annealing temperature for several different initial Ti-deposition amounts. Each film was annealed sequentially in 50–100° increments and held at each temperature for 10 s. This procedure leads to a total heating time between 800 and 1050 K of 60 s. The Ti concentration was determined from He⁺-ISS peak intensities using Eq. (1). The general behavior observed can be divided into three regimes: sub-DU, single-DU and multi-DU films.

The annealing curves in Fig. 3 from Ti films corresponding to 0.87 and 0.93 DU deposited on Pt(111) decrease slightly upon annealing between 400 and 700 K and then drop rapidly by 950 K. No further changes were observed for higher annealing temperatures up to 1100 K. It is quite possible that the small decrease in Ti signal observed at lower temperatures may be due to restructuring of the film rather than interdiffusion.

No change in the surface Ti concentration was observed for 1-DU Ti films until an annealing temperature of 750–800 K was reached. The Ti concentration then decreased rapidly as the temperature was increased to 1000 K. The annealing behavior for these curves was different from that of thinner films, though at higher temperatures their behavior was similar. It is interesting that the temperature window for

interdiffusion in a 1-DU Ti film observed here is consistent with the process parameters reported by Sreenivas et al. [22] who saw no Ti diffusion in Ti/Pt bilayers annealed in O₂ at 200 °C but significant changes at 650 °C.

Ti films greater than 1-DU deposited on the Pt(111) surface showed no changes in the topmost surface concentration until a temperature of 800 K was reached for a 2.5-DU film and 1050 K for a thicker, 5.0-DU film. At temperatures higher than 1050 K, inter-diffusion occurred rapidly as shown by the steep drop in Ti signal.

The origin of the stability of Ti films on Pt comes from the lower surface free energy of Ti than Pt (2050 mJ/m² versus 2550 mJ/m² at $T=0$ K) [34], and the larger radius of Ti atoms than Pt atoms (1.46 Å versus 1.39 Å). Nevertheless, alloying is strongly exothermic because Ti and Pt form strong intermetallic bonds. Ruban et al. [35] proposed from first principles calculations that there is a strong driving force for anti-segregation (alloying) of Ti on a Pt(111) surface. Therefore, interdiffusion occurs at relatively low temperatures and allows Ti to maximize the number of Pt neighbor atoms.

We used XPS to determine the chemical state of a 1-DU Ti film after heating. Fig. 4 shows XPS spectra of the Ti 2p core level for a Ti/Pt(111) alloy surface (1 DU annealed to 1000 K) and a thick Ti film (6 DU) deposited on Pt(111) at 300 K. Background subtraction and curve fitting were done using the SpXZeigR routine available for Igor Pro (WaveMetrics) by assuming a 2p_{1/2}/2p_{3/2} intensity ratio of

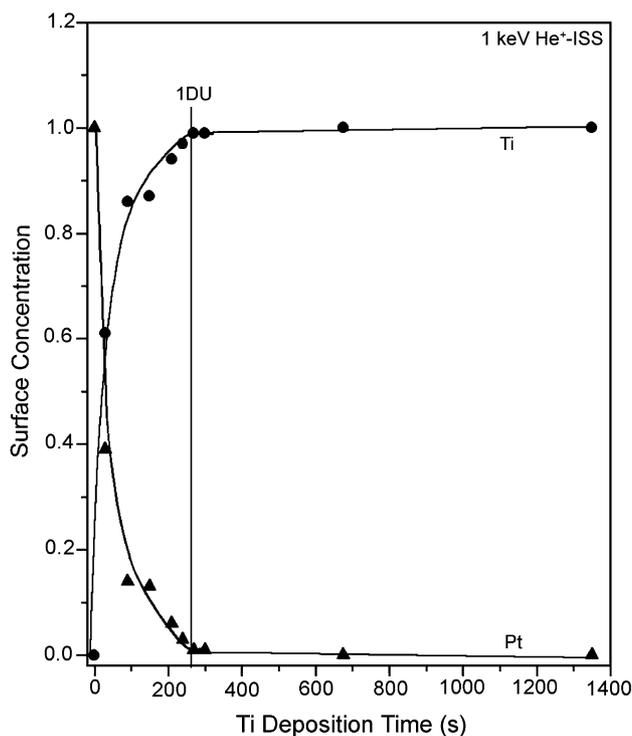


Fig. 2. Kinetics of Ti film growth on Pt(111) at 300 K as probed by using He⁺-ISS. The Pt(111) surface is completely covered by Ti after a deposition time of 270 s. This amount of deposited Ti is defined to be 1 DU.

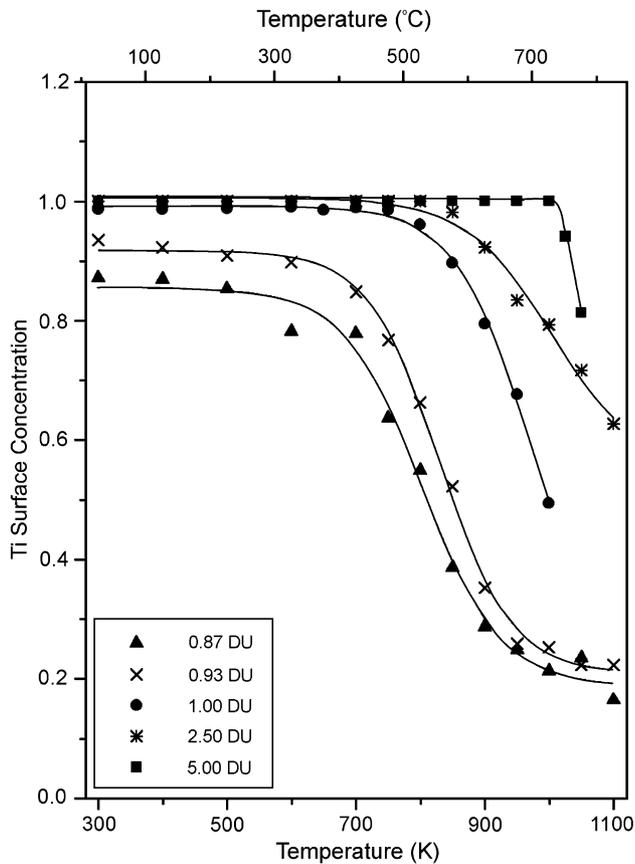


Fig. 3. He⁺ ISS results for Ti films of different thicknesses deposited on Pt(111) at 300 K and annealed. The films were annealed sequentially in 50–100° increments and held at each temperature for 10 s. Interdiffusion of Ti films less than 1 DU starts at temperatures as low as 700 K. For 1-DU Ti films, diffusion begins at 750–800 K. For thicker Ti films of 2.5 and 5.0 DU, Pt is not detected at the surface until temperatures of 800–1050 K are reached.

1:2 for both curves and a lineshape for both curves that best fit the Ti thick film spectra, while allowing the spin-orbit splitting $\Delta(2p_{3/2}-2p_{1/2})$ in the two curves to vary if necessary. Within the short time (5 min) required for an XPS scan, there was no detectable oxygen contamination for the thick Ti film. A longer acquisition time of 50 min was used for the alloy surface and still no oxygen was detected. The Ti $2p_{3/2}$ peak from the alloyed film occurred at 456.7 eV BE, which is shifted 1.5 eV to higher binding energy relative to that from the thick, pure Ti film. The $\Delta(2p_{3/2}-2p_{1/2})$ splitting in both cases was 6.0 eV. These results are consistent with a study by Ringler et al. [36] that focused on alloy formation of Ti on Pt(111). Also, Chen et al. [37] showed that the Pt 4f and Ti 2p core levels were shifted by 0.4 and 1.3 eV, respectively, to higher binding energies for the bulk Pt₃Ti(111) alloy surface compared to the pure, single-component metals. Given this good agreement of our data with previous work, we chose to not make a detailed analysis of the relatively small, Pt core-level shift upon alloying because of the dominant unshifted contribution in our alloy spectrum from unalloyed Pt in the crystal.

Our experiments on the thermal stability of Ti films on a Pt(111) single crystal under UHV conditions extend previous studies that focused on interdiffusion at Ti/Pt interfaces in model device structures, and provides benchmark data for understanding these more complicated systems. For example, Olowolafe et al. [25] examined the effect of process conditions on the stability of Pt/Ti/SiO₂ interfaces. Mixing between layers was shown to occur in samples annealed in N₂ or O₂ at 500–800 °C. In a separate study by Sreenivas et al. [22], no changes in Ti/Pt films were found after annealing at 200 °C for 8 h in O₂, but significant changes were observed after annealing at 650 °C in O₂ for 30 s. They attributed this to diffusion of Ti through Pt grain boundaries. However, we have observed that even for a Pt(111) single crystal which has no grain boundaries (nominally), and even in the absence of O₂, interdiffusion in Ti films can start at temperatures below 500 °C. Therefore, it appears that the thermal instability in Ti/Pt interfaces is a bulk-materials property. Hence, lower process temperatures, different materials, or possibly additional barrier structures will be necessary to eliminate the interdiffusion problems associated with Ti/Pt bilayers.

Our studies provide a more precise temperature for Ti/Pt intermixing to happen at a (111)-oriented interface than either of the practical studies mentioned above which used anneal-

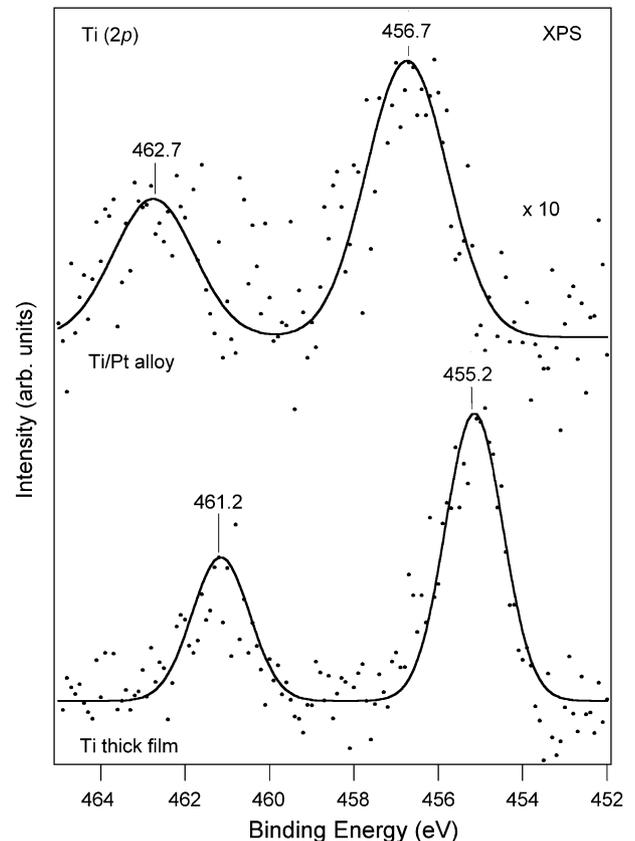


Fig. 4. Core-level XPS spectra for a 1-DU Ti film on Pt(111) annealed to 1000 K, and for a thick Ti film deposited on Pt(111) at 300 K. The Ti peak was shifted 1.5 eV to higher binding energy for the alloy compared to the thick Ti film showing a strong electronic interaction due to Pt–Ti alloying.

ing temperatures that were derived from processing conditions for particular device structures. We show that the onset of interdiffusion occurs at 700 K (427 °C). This temperature is consistent with these previous studies, but provides more fundamental information for processing considerations.

Finally, Sreenivas et al. [22] commented that the thermodynamic driving force for Ti out-diffusion through Pt films was the formation of TiO_x. This undoubtedly contributes favorably to the energetics in practical systems. However, we constructed our model system with Ti deposited on top of Pt, resulting in thermal diffusion of Ti into the bulk of the substrate and carried out the annealing experiments rigorously in the absence of O₂. Thus, we know that Ti transport into Pt, in our studies, is not driven by TiO_x formation, but by strong Ti–Pt bonding interactions. This driving force is alone sufficient to cause thermal instability at Pt–Ti interface above 700 K.

4. Conclusions

Our results establish that strong Pt–Ti intermetallic bonding provides sufficient driving force for thermal interdiffusion of Ti and Pt at a (111)-oriented interface to occur at temperatures as low as 700 K (427 °C) under ultrahigh vacuum conditions, i.e., rigorously in the absence of oxygen, and with a minimal influence of grain boundaries. We make this conclusion based on our He⁺-ISS studies of the effects of vacuum annealing on Ti films deposited on a Pt(111) single-crystal substrate. Ti films less than 1 DU were stable on the Pt(111) surface up to 700 K, with only a slight reduction in surface-Ti concentration observed for lower temperatures. Annealing at higher temperatures caused the surface Ti concentration to decrease and very little Ti was left in the topmost surface layer after heating to 950 K. For Ti films of 1 DU, interdiffusion began between 750 and 800 K. For thicker films, greater than 1 DU, heating to temperatures of 800–1050 K caused sufficient interdiffusion to effectively remove Ti from the outermost surface layer. After annealing, XPS showed a chemical shift for the Ti(2p) peak of 1.5 eV to higher binding energy, providing evidence of Pt–Ti alloy formation.

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