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Titanium films were deposited on quartz, glass, polyamide and PET substrates in a high vacuum system at room temperature and their electrical resistance monitored *in vacuo* as a function of thickness. These measurements indicate that a low electrical resistance layer is formed in a gas-solid reaction during the condensation of the initial layers of Ti on glass and quartz substrates. Layers begin to show relative low electrical resistance at around 21 nm for glass and 9nm for quartz. Samples deposited on polyamide and PET do not show this low resistance feature. © 2016 Author(s). *All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* [http://dx.doi.org/10.1063/1.4963679]

The motivation to study the titanium silicides system rests on the problem of producing low dimensional electrical contacts for ultra large-scale integration devices.[1] This motivation and the industrial potential of these materials have led to various studies on the interaction of Ti with crystalline Si, mostly at high temperatures (~700 °C in inert atmosphere), showing the formation of low electrical resistivity silicides.[2–4]

The optical properties of these low-dimensional conductors may also be of interest in those experiments requiring transparent substrates, in which case glass or quartz is often used, a use that may be boosted with the introduction of flexible glass by Corning®.[5] Additionally, the growth of low dimension contacts is of interest for flexible electronic devices. There is a report on spontaneous growth of low dimension (2D) single crystalline $TiSi_2$ nanonets by means of chemical vapor deposition at 675°C.[6] Resistivity of this nanostructure was approximately $10\,\mu\Omega cm$, smaller than that reported for $TiSi_2$ bulk of around $15\,\mu\Omega cm$.[7] Titanium silicide formation with low resistance has been reported for samples grown on silicon wafers[1] by means of thermal evaporation, with wide spread resistivity values ranging from 15 up to $100\,\mu\Omega cm$ depending on the proportion of low resistivity phase (C54) with respect to the high resistivity phase (C49 or C40). That proportion depends strongly on the annealing temperature that is usually around 600°C.[8–10]

This indicates that process conditions are critical for the preparation of such materials in which stoichiometry, morphology, structure, substrate preparation and thermal processing are key features to obtain low resistivity samples. Furthermore, to improve the stability and resistivity of samples, one of the most common methods is the addition of refractory metals by ion implantation.[7]

Interestingly, a recent study reported the detection of Ti-Si bonding during the atomic layer deposition of TiO_2 onto hydrogen terminated silicon at a moderate temperature of 100°C; the XPS results show evidence of the bonding type at the Si/TiO_2 interface.[11] This report motivates our study of titanium on glass and quartz substrates, materials that are commonly used for metallic thin film studies, but the possible reaction of the sample and the substrate at their interface is usually not taken into account.

Our main objective in this work is to report the electrical properties of the interface of titanium with glass and quartz substrates during the deposition of thin films due to the possible interaction of the titanium gas arriving and condensing onto the silica surface.

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The films were deposited by electron beam evaporation from titanium pellets with a 99.99% nominal purity (Sigma-Aldrich) onto boro-silicate glass microscope slides from Paul Marienfeld GmbH & Co, quartz (SPI Supplies), PET and polyamide (Kapton®). Prior to deposition the glass and quartz substrates were cleaned by applying sequentially acetic acid, distilled water, sulfochromic solution distilled water and acetone. PET and polyamide substrates were rinsed in distilled water. 70 nm copper electrodes were placed for electrical resistance monitoring.

Evaporation of the titanium films was carried out at a base pressure of around 8×10^{-7} Torr with a rate of about 0.1 nm/s. The deposition was done at room temperature and no annealing treatment was applied after deposition. In situ electrical resistance was monitored using an Agilent 34972A system in the four-probe method configuration with an acquisition rate of 1 data point per second. Electrical resistance samples were typically about 1 cm in length and 1.5 mm wide.

Thickness was determined by means of a 6 MHz quartz crystal microbalance (Maxtek TM-400). Some samples were made by covering the substrate with approximately 200 nm of Ti so as to have a relatively pure Ti sample with near bulk characteristics for comparison purposes. Twin samples were shuttered at the time of electrical resistivity detection to study the stability of the low resistivity phase and for *ex situ* characterization.

Representative sample results of the *in vacuo* monitored electrical resistance measurements as a function of sample thickness during growth are shown in Fig. 1. The upper curves show the resistivity of the samples grown on Kapton and PET while the lower curves show that of the samples grown on glass and quartz. The most striking feature of the sample on quartz is its initial low resistivity value which occurs at 8.4 nm, its percolation threshold; it is about one twentieth of that of the 200 nm thick Ti film, which has a value similar to that reported for similarly grown Ti samples.[12–14] Its low value and its subsequent increase indicate that the first few layers of the deposited Ti are heavily influenced by a reaction with the SiO_2 substrate at their interface, possibly forming a low conductive phase of titanium silicide. This suggests that the initial low-resistivity film formed at the Ti-quartz interface is very thin. Thicknesses of a few monolayers of this material formed on Si samples have been reported by several authors.[2,11,12]

To our knowledge, this anomalous room temperature behavior has not been reported before. The deposition rate plays a critical role in order to detect the phenomena; we also have observed the same effect for zirconium thin films prepared under similar conditions. Table I shows the average threshold
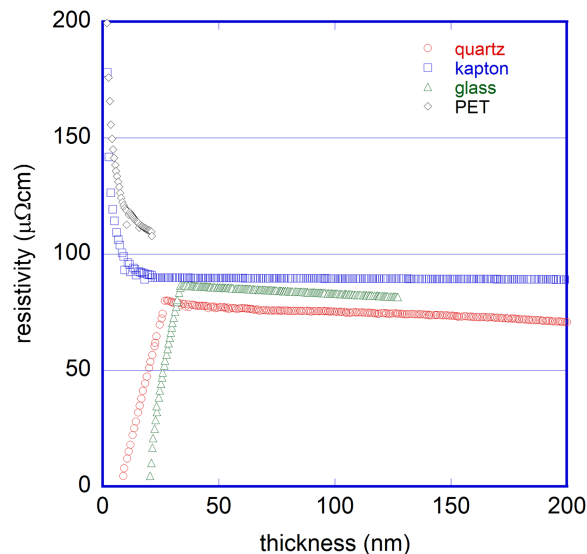

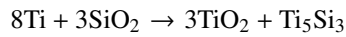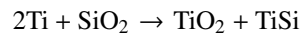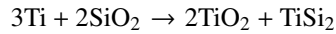FIG. 1. Resistivity of Ti films as a function of thickness on different substrates. On kapton[(R)] and PET the resistivity show the expected behavior, decreasing as more Ti arrives of the substrate. On glass and quartz the resistivity indicates the formation of a high conductivity film in the initial stages. The upper end of the resistivity axis has been limited to make the changes more obvious.

TABLE I. Average initial resistivity values and threshold thickness for Ti films on various substrates.

Substrate	Resistivity ($\mu\Omega$cm)	Thickness (nm)
Quartz	3.7 ± 0.2	8.9 ± 0.5
Glass	4.7 ± 0.5	21.1 ± 0.5
PET	4100 ± 1	0.65 ± 0.5
Polyamide	8500 ± 1	0.64 ± 0.5

conductance thickness for Ti on different substrates. We find initially low resistivity values for quartz and glass and high values for those on polyamide and PET.

There are several probable reactions that form thermodynamically stable compounds;[15] some of the reactions in which stable products can be formed may be as follows:

$$3Ti + 2SiO_2 \rightarrow 2TiO_2 + TiSi_2$$
$$2Ti + SiO_2 \rightarrow TiO_2 + TiSi$$
$$8Ti + 3SiO_2 \rightarrow 3TiO_2 + Ti_5Si_3$$

One can argue that due to the fact that silica surfaces posses a high number of dangling bonds and defects,[16] the arrival of titanium in the gas phase reacts with the lose oxygen on the surface leaving the silicon unpaired, which reacts with the following oncoming titanium atoms forming a Ti-Si bond as observed by Chen.[4] In addition, Ti atoms on the surface diffuse at room temperature into the silica,[2,12] supporting the hypothesis of a silicide type compound. Another important aspect is that the average value in which the conductivity threshold thickness occurs, 8.9 nm on quartz and 21 nm on glass, is equivalent to roughly 3 to 6 atomic layers respectively, and these layers are too few, under our vacuum conditions, to form a continuous titanium layer on the substrate, which suggests that a reaction at the inter phase metal-substrate is taking place.

There are two more possible explanations for the formation of the low resistivity layer. First the formation of a titanium sub oxide type phase with low resistivity, like Ti_3O_5 that at room temperature has a 32 $\mu\Omega$cm resistivity[17] or, second, a Si-Ti sub oxide with very low resistivity due to the oxygen deficiency at the surface when the titanium is deposited.

Regarding the stability of the compound, its electrical low resistance is maintained while the sample is kept under vacuum conditions. The effect of venting the chamber increases the resistance of the samples rapidly from their lower value of about 4 $\mu\Omega$cm to 100 $\mu\Omega$cm.

The *ex situ* Raman spectrum in Fig. 2, confirms the presence of TiO_2 as a product of the oxidation of the sample during venting, additionally, the Raman spectrum in which the signal to noise ratio could not be improved to be better than 7:1 gives some additional indication of the presence of titanium silicides beside the TiO_2 signal in agreement with other authors.[18–20] In this region, the substrate does not show any structure other than a background signal that contributes to the intensity observed. None of the other *ex situ* characterizations tried gave conclusive evidence of the compound formed during deposition. Further work is being done to determine the nature of the compound.

As the film grows in thickness it is expected that its electrical resistivity should decrease as the effect of surface scattering of electrons becomes relatively less important, the grains become larger and the contacts among them increases. We observed this behavior in the resistivity of our samples grown on polyamide and PET. However, the resistivity values of films deposited on quartz and glass, after the initial low resistivity, show an increase (see lower curve of Fig. 1) before the expected decrease, which begins at approximately 27 nm for quartz. This could be the result of inter-diffusion of Ti and the initially formed silicide, leading to an increase of impurity scattering of the charge carriers, as proposed by Iwami *et al*.[13] for the case of Ti deposited on Si(111) at room temperature. Another possible explanation is growth of the sample in a form analogous to a Stranski-Krastanov (SK) mode, that is, a two stage growth: a continuous silicide phase of about 9 nm for quartz (as explained above) followed by a second stage of strain inducing metallic Ti islands on the silicide layer. This Ti island on silicide structure may lead to the creation of dislocations as a stress relief mechanism in the SK model, thus increasing the electrical resistance of the system. At thickness values above an average value of 27 nm the resistance is governed by the increasing Ti coverage, showing the expected decrease in
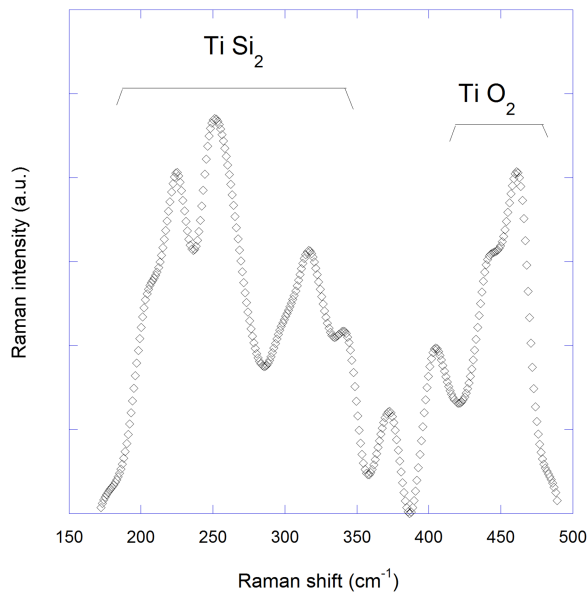
FIG. 2. Ex-situ Raman spectra of a 8.4 nm sample grown on quartz. The region in which the reported data for $TiSi_2$ of different phases and TiO_2 are shown as a reference.

resistivity values as the thickness of the film increases as shown in Fig. 1. At this thickness the Ti island structure on the silicide coalesce to form a continuous film. This produces the sharp transition in the resistivity curve shown in Fig. 1.

Cai *et al.*[21] studied the surface structure of Ti deposited on glass substrates at various evaporation rates and thicknesses, the thinness sample being 100 nm thick. The XPS measurements on this sample does not show a Si signal until the interface between the sample and the substrate is reached, but does show a Ti signal in the substrate just below the interface. This is the possible region of the formation of the low resistance film through a gas phase reaction of the metal with the substrate at room temperature.

To summarize, we deposited Ti films on glass and fused quartz at room temperature and found that a low resistance conductor is initially formed at the SiO_2 interface in contrast with samples deposited on PET and polyamide which show the initial usual high resistivity behavior. From the low resistivity values measured, the thermodynamic analysis of the probable reactions that may occur on the quartz or glass surface and the Raman spectrum observed in the corresponding wavelength range, we are lead to conclude that room temperature formation of low resistivity $TiSi_2$-like film has formed. Although the material is not stable at ambient pressure, in light of the resent advances on stabilization of $TiSi_2$ films by addition of refractory materials, this material may find technologically important applications.

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