

An XPS study on ion beam induced oxidation of titanium silicide

P. Osiceanu

“I.G. Murgulescu” Institute of Physical Chemistry, Splaiul Independentei 202, Bucharest 060041, Romania

Abstract

Titanium silicides (TiSi₂) films grown on Si(1 0 0) substrate were investigated by ex situ XPS depth profiling after athermal ion beam induced oxidation (IBO) at 12 keV O₂⁺ incident energy and normal incidence. The composition and stoichiometry of these films were quantitatively determined as chemical state relative concentrations versus sputter time. “In depth” silicon and titanium oxidation states have been obtained after spectra deconvolution, showing a mixture of silicon dioxide, titanium dioxide, titanium suboxides, elemental titanium and residual traces of titanium nitride. Thermochemical data based on the corresponding enthalpies of formation of the oxides cannot explain our experimental results as in the case of low energy IBO, an oxygen defective altered layer is formed, presenting features of a reduced TiO_x phase.

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1. Introduction

3D serie metal silicide layers have become widely used in VLSI technology as interconnect material, gate electrodes and, recently, nanowire structures [1]. The chemical stability and reasonably low temperatures of formation as well as the low resistivities ($-15 \mu\Omega \text{ cm}$), good process compatibility with Si, good contact to other materials are among the most important advantages of these materials. Low energy oxygen ion beam sputtering in the keV range is routinely applied for sputter depth profiling of these films mainly in SIMS analysis technique. It is widely accepted that the sputtering process during depth profiling leads to surface and subsurface compositional changes [2]. The oxide formation might induce effects like changes in ionization yields, segregation, etc., and the energy transfer from the primary ions will induce atomic displacements and hence, profile distortions through a series of collision cascades. A higher quantification accuracy and a better depth resolution can be achieved by improving our basic understanding of the sputter induced phenomena (ion incorporation, sputter yield, compound formation, atomic displacements, bond breaking, surface defects formation, etc.). Under these circumstances, the XPS depth profiling measurements on chemical changes at surface and near surface region will improve our knowledge of

these sputter induced phenomena giving us a better insight on the oxidation process itself for such materials. In this paper, we focus on a detailed and accurate investigation of the chemical “in depth” composition of a thin titanium silicide layer athermally oxidized by low energy oxygen ion beams.

2. Experimental

The initial sample was prepared by Ti evaporation on Si substrate and subsequently annealed by means of rapid thermal processing. In this way, a TiSi₂ polycrystalline film was obtained with thickness of about 300 nm [3]. The initial sample TiSi₂ has been athermal oxidized by O₂⁺ ion beam 12 keV normal incidence, rastered over 2 mm × 2 mm surface and analyzed by RBS nondestructive technique, while XPS measurements were performed “ex situ” in a depth profiling experiment. The total input power from the ion beam at this energy holds below the limit for ion beam induced heating. The “as-received” sample has been loaded into the XPS spectrometer and sputter etched in situ with Ar⁺ ions of current density of 20 mA/cm², 2.5 keV kinetic energy at normal incidence, focused on 300 μm and rastered over the same 2 mm × 2 mm surface for different periods of time up to 10 min. The aim of this etching process was to remove the oxides for a “layer by layer” in depth analysis. The XPS measurements were performed on a SSX-100 equipment, a UHV apparatus at a pressure -10^{-8} Pa using a monochromatic Al K α X-ray source

E-mail address: posiceanu@yahoo.com.

(1486.6 and 0.7 eV overall resolution) and facilities for “in depth” Ar^+ ion bombardment. Sputtering conditions were assumed to be comparable to a sputtering rate of 2 nm/min determined by measurement of a standardized layer of SiO_2/Si . The 1s peak of carbon with a binding energy (BE) of 284.6 eV was used as reference in the as received and briefly sputtered samples in which less than 10 nm was removed. On further sputtering, the N 1s was taken as reference assuming no change in its BE value. The spectrometer was previously calibrated by assuming the binding energies (BE's) of the Au 4f7/2 line is 84 eV, Ag 3d5/2 line is 368.27 eV and Cu 2p3/2 line is 932.67 eV with respect to Fermi level [4]. The standard deviation in the BE value is lower than 0.2 eV. Survey scans (0–1100 eV) were recorded for each sample as well as high resolution scans over narrow energy ranges around each peak of interest: C 1s, N 1s, O 1s, Ti 2p and Si 2s. The raw spectra were then smoothed and fitted with a non-linear least-square fit program using Gauss–Lorentzian peak shapes after the appropriate Shirley background subtraction. The fitting procedure included four parameters: peak position, full width at half maximum (FWHM), Gaussian–Lorentzian mixture ratio and intensity ratios lines constraints. Regarding energy scale calibration and data management and processing, we followed the recommendations of ISO-Technical Committee 201 (“Surface Chemical Analysis”).

3. Results and discussion

The film composition was estimated by XPS measurements from the relative area intensities of different high resolution peaks after normalizing with respective relative sensitivity factors and after corrections for transmission function, escape depth and detector efficiency. During this XPS, depth profiling analysis over 100 sputtering cycles were performed proceeding from the top surface, subsurface to the “bulk” of the oxidized layer and through interface to the bulk of the initial titanium silicide substrate. XPS spectra were recorded after every sputtering cycle. For quantitative in depth analysis as element relative concentrations (atom%), both survey scan spectra and high resolution core-level spectra have been used following the models outlined by Seah [4]. This analysis gives evidence that in the first 15–20 atomic monolayers Ti is found with a higher

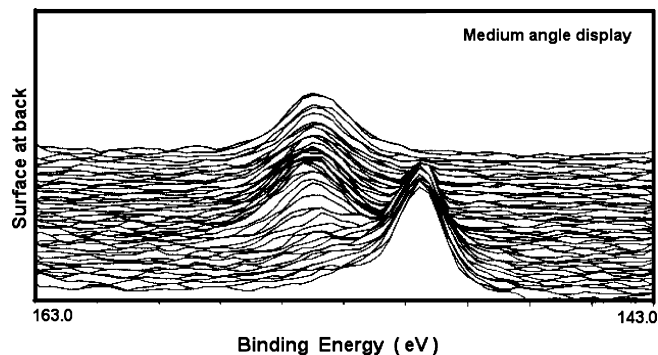


Fig. 2. Depth profiling (“3d projection”) XPS 2s spectrum of silicon.

concentration (–25%) in comparison with subsurface region where the amount of Ti decreases to –15% in close agreement with RBS results [2]. This Ti enhancement towards the surface of the altered layer can be explained by preferential sputtering of Si during ion beam oxidation in the above mentioned conditions. A close inspection of these spectra (“3d projection” XPS spectra of Ti 2p, Si 2s and O 1s, Figs. 1–3) reveals the main features of the oxidized sample: a thin oxide layer is followed by the interface which is rather sharp and then by the bulk of the original TiSi_2 sample where Ti and Si appear as in their elemental form, i.e. the BE's are found, practically, unaffected by alloying. Starting the analysis just in this stage an “expert eye” can notice that Ti shows, in the oxidized region, a band-like spectrum suggesting the presence of suboxides together with full oxidized and elemental titanium, the latter featuring characteristic photoelectron line spectra chemically shifted by about 5 eV according to the reference data [5]. Silicon “3d projection” spectrum (Fig. 2) shows characteristic line spectra associated to its full oxidized state found through the entire oxidized layer, shifted by about 4 eV to higher BE's relative to that of the elemental Si from TiSi_2 , according to the above mentioned reference data. Regarding oxygen incorporation, the in depth XPS spectrum (Fig. 3) reveals a large amount of oxygen localized in the first atomic layers mainly as a result of the increasing of the stopping power due to densification of the altered layer, although the backscattering of the implanted oxygen towards the surface as well as recoil implantation of adsorbed oxygen atoms into the subsurface cannot be ruled out. Initially, the oxygen irradiation of the sample leads to a large

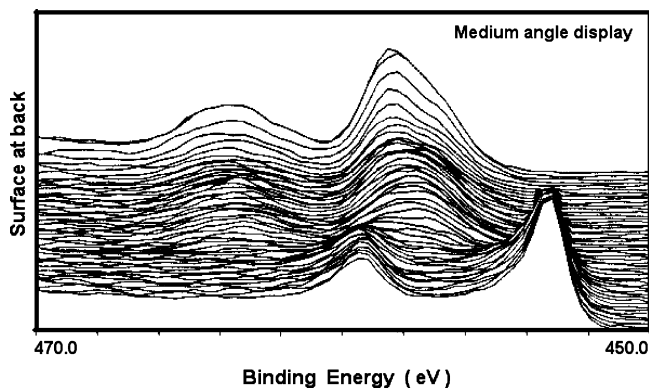


Fig. 1. Depth profiling (“3d projection”) XPS 2p spectrum of titanium.

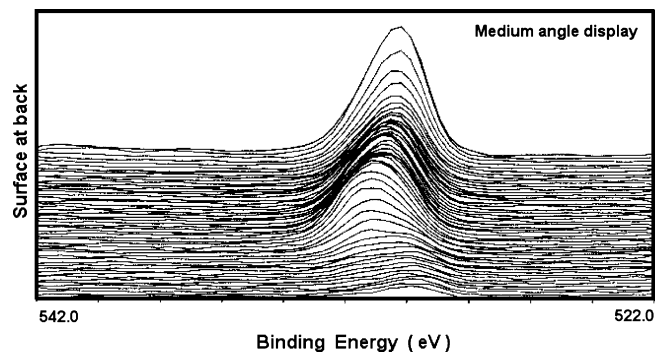


Fig. 3. Depth profiling (“3d projection”) XPS 1s spectrum of oxygen.

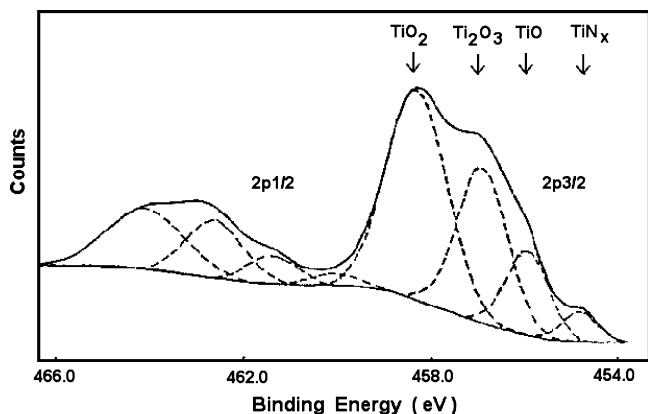


Fig. 4. Ti 2p photoelectron deconvoluted spectrum in TiSi₂ ion beam oxidized after 52 sputtering cycles.

incorporation of the oxygen into the matrix followed by an amorphisation of the target and reaching a stationary level with a complete compound formation. At this stage, the sample was analyzed by RBS and a complete silicon oxidation has been confirmed. To allow an accurate analysis of the sample's "in depth" chemistry, some high resolution photoelectron spectra have been picked-up from the "3d projection" spectra following all the characteristic regions: surface, subsurface, oxidized layer, interface and TiSi₂ substrate. Fig. 4 shows one of the Ti XPS photoelectron spectra, drawn out from the depth profiling spectra (Fig. 1), after deconvolution procedure. The Ti 2p transition from 452 to 468 eV has been reconstructed using eight Gaussian–Lorentzian components to fit the entire envelope. The Ti 2p photoelectron line is split into two components 2p3/2 and 2p1/2 according to split-orbit coupling. Every component is fitted with four curves showing titanium nitride (TiN_x), two suboxides (TiO and Ti₂O₃) and titanium dioxide (TiO₂). The components required to make the fit to the experimental data are the same in either case selected from the in depth profiling analysis, the elemental titanium (Ti in TiSi₂) appearing when the Ar⁺ beam proceeds into the bulk of the sample. A short comment related to the presence of a small amount of titanium nitride would be worth discussing at this point. The N 1s photoelectron line has been recorded over the entire analysis showing an accumulation of the nitrogen up to 4% into the bulk of the sample. A question arises: where from nitrogen in our system with, initially, 10⁻⁹ Pa in the analysis chamber, 99.9999% Ar purity and after 10 cycles of purging of the gas handling system? Even if the nitrogen is present in very low concentration in our system (perhaps mainly because the purging process was not fully completed or even because of some traces of nitrogen in the residual atmosphere), the titanium proves to be very reactive (the sticking coefficient is close to unity) trapping every nitrogen atom found in its neighbourhood by ion incorporation. Therefore, much care must be paid by the experimentalist working with titanium-based samples in high and even ultrahigh vacuum conditions. Silicon, which is less reactive than titanium, does not show the formation of the nitride. Fig. 5 exhibits the Ti chemical state relative concentrations versus sputter time showing titanium in

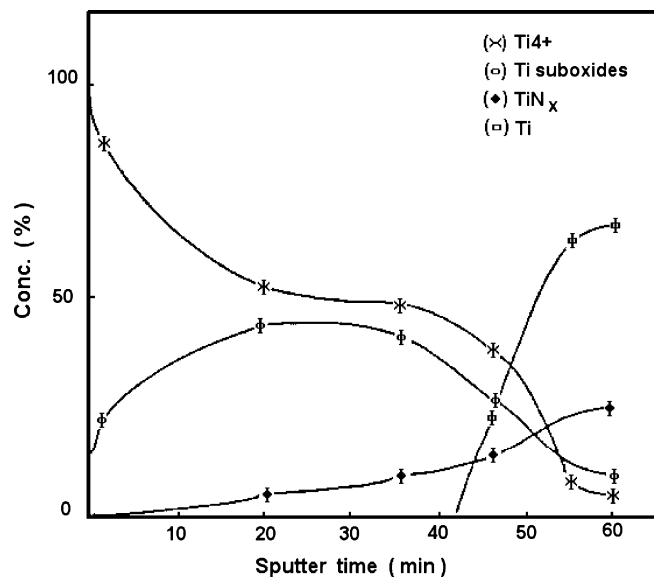


Fig. 5. Ti chemical states relative concentrations vs. sputter time.

its full oxidized state, titanium suboxides, elemental titanium and a small amount of titanium nitride which is accumulated into the "bulk" of the oxidized film following the same trend observed during N 1s photoelectron line recording. In the near surface region, titanium full oxidized (4+ oxidation state) is the dominant feature, but proceeding into the "bulk" of the oxidized film the contribution of the suboxides increases (> 40%) over a large range into the sample's depth profile. In the interface region, which is rather sharp for the particular oxidation process involved all the oxidation states are present together with elemental titanium and ~8% titanium nitride. Fig. 6 shows the distribution of the chemical states into the sampling depth but for silicon. The oxidation process of silicon exhibits a rather different behaviour. The full oxidized silicon (4+ state) can be noticed over a large range of the sampling depth while the contribution of the suboxides is maintained to a

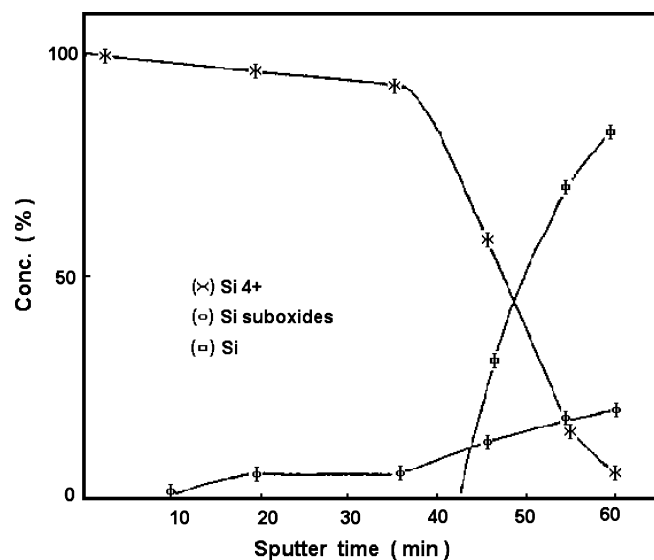


Fig. 6. Si chemical states relative concentrations vs. sputter time.

low level (< 5%) up to the interface region. The stoichiometry and the electronic structure of the silicon induced ion oxide are very close to a thermal oxide as can be found additionally from XPS valence band measurements [6]. During wet oxidation, TiO_2 is thermodynamically favoured above SiO_2 as the formation free enthalpy is more negative (−938.7 and −910.6 kJ/mol, respectively [7]). However, our findings derived from experimental measurements cannot be explained by thermochemical data. Both theoretical calculations on electronic structure of titanium oxide and experimental inverse photoemission (IPE) measurements reveal that in the case of ion bombarded titanium surface, some spectral changes appear that are typical of a defective surface being characteristic of a reduced TiO_x phase [8]. Indeed, it is expected that a variety of defect configuration are formed at the near surface upon ion bombardment. In this respect, we can consider that since at the sites where some point defects (oxygen vacancies) appear, there will be induced a negative charge leading to a changing from Ti 4+ to Ti 3+ or lower oxidation states in order to maintain the local charge neutrality and thus, producing an oxygen deficient TiO_x region. On the other hand, at normal incidence, in the keV O_2^+ range the sputter yield is very low, typically 0.2–0.4 atoms/ion leading to a high oxygen incorporation. Consequently, an excess of oxygen should be available causing not only the oxidation of the most favourable element but also the oxidation of the other metals atoms as well. The bulk of the film was found to be titanium silicide with the same stoichiometry as the starting sample TiSi_2 prior to ion beam oxidation and in agreement with RBS measurements.

4. Conclusions

XPS depth profiling analysis is a powerful tool complementary to RBS and SIMS methods getting detailed information on the stoichiometry and chemical composition of the surface layer modified under O_2^+ bombardment at 12 keV primary energy and normal incidence. Under these conditions, a surface accumulation of Ti is found as a consequence of preferential sputtering of Si. A detailed in depth XPS chemical analysis leads us to the conclusion that a heterogeneous layer is

formed consisting of a mixture of silicon dioxide, titanium dioxide, titanium suboxides and elemental titanium without a strict overlayer/substrate structure. Some residual traces of titanium nitride occurred indicating a very high reactivity of titanium, even in titanium silicide and UHV conditions. Our findings derived from experimental measurements cannot be explained by thermochemical data, since in the case of ion bombarded TiSi_2 sample, some spectral changes appear that are typical of an oxygen defective surface being characteristic of a reduced TiO_x phase. Much work has to be furthermore performed on energy and angular dependence for IBO on these materials to gain a better insight on the steps involved in this particular oxidation process: ion incorporation and retention, bond breaking and reaction in order to prove some potential advantages over conventional thermal oxidation and for improving quantitative SIMS, XPS and AES analysis.

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