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Ion mass interferences and matrix effects on SIMS depth profiling of thin Ti/Si multilayer films induced by hydrogen, carbon and oxygen contaminations

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Abstract

Secondary ion mass spectrometry (SIMS) with argon beam has been used to determine the depth profile of ultra-thin Ti/Si multilayer system deposited on crystalline silicon wafers by laser ablation of titanium and silicon targets. The redistribution of elements in the structure has been studied after subsequent high temperature (HT)-treatment, what leads to uniform metastable phase of the composite films. The data obtained by positive atomic ion detection generated from sample before HT process show anomalous behavior of titanium distribution. We discuss the influence of contaminations on the results and attribute apparent Ti^+ signal in Ti/Si-based films to numerous ion mass interferences and matrix effects present during sputtering of the multilayers. The negative SIMS analysis in conjunction with detection of sputtered TiO_2^- and Si_2^- molecular species is proposed for depth profiling of Ti/Si to avoid artifacts in Ti and Si profiling, respectively, caused by the presence of contaminations in the multilayers.
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Keywords: SIMS; Matrix effects; Mass interferences; Ti/Si multilayers; Titanium silicides

1. Introduction

Transition metal silicides are interesting for electronic application and are widely used in ultra-large-scale integrated electronic circuits (ULSI) as Schottky barriers, ohmic contacts and interconnects [1]. The interest lies in their low resistivity [2] and usefulness due to hardening response [3]. Composite material based on ultra-thin Ti/Si multilayer films is belonging to this group providing its promising application in optoelectronic sensors [4]. However, sub-nanometer characterization of such materials is essential because plays important role in monitoring the production and optimizing properties of conductive films.

Secondary ion mass spectrometry (SIMS) is often used to obtain the elemental depth profiling, although this is difficult in ultra-thin materials. High depth resolution is required for these ultra-thin layers, so a low or ultra-low primary ion energy should be applied to reduce atomic mixing during sputtering [5]. The most important complications of the SIMS elemental monitoring are ions mass interferences and matrix effects [6,7]. As a result, the data interpretation becomes not straightforward, since Ti^+ and Si^+ profiles reflect the distribution of impurities in examined structure. The prevailing thought about the origin of such matrix dependence is that the existence of electronegative species (e.g., oxygen) in the sample emphasizes the positive secondary ion intensity during sputtering. In other words, varying O amount in the structure leads to different ionization probabilities, and what follows the sputter yield changes of the monitored species. Therefore, the quantitative depth profile of Ti-silicides in the presence of a contaminants and matrix dependence is difficult. In addition, titanium is extremely reactive and thus oxygen (or other impurities) from the ambience can be easily incorporated into the Ti-based layer and affect the silicidation process.

Attempts to overcome the matrix effects rest on reducing them only insignificantly. The use of Cs^+ as primary ion beam and the detection of the molecular MCs^+ (where M is the element of interest) was found to be a useful technique

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for quantitative SIMS analysis [8–10]. Dümmler et al. [11] showed that oxygen flooding should not be employed in Cs^+ SIMS measurements of Ti/Si as it leads to numerous mass interferences. Also an energy-filtering technique can be used to effectively reduce matrix effects in SIMS of metal silicides [12].

The sputtering mechanism of very thin Ti/Si multilayerd films is complex and is not yet fully understood due to matrix effects, mass interferences, interface effects, surface roughness and atomic mixing.

The objective of this study is to find pertinent conditions of SIMS for depth profiling of fabricated sub-nanometer Ti/Si multilayered systems. In this work we try to explain the observed features of the SIMS analysis in terms of common matrix dependence and ion mass interferences caused by contaminations embedded in Ti/Si multilayer thin films (including oxygen, carbon, hydrogen and fluorine). The intermixing of multilayered films, change of the structure and element redistribution after high temperature treatment have been studied in aspect of Ti-silicide formation.

2. Experimental

The samples were fabricated by laser ablation of the titanium and silicon targets on silicon ⟨1 0 0⟩ substrates. The periodic structure consists of four Ti/Si bilayers (a bilayer period of 17.6 nm with Si film of 1.8 nm thick). The thickness and composition of fabricated films were controlled in situ counting of the excimer laser pulses at wavelength of 193 nm and ambient gas pressure (nitrogen in the case of capping layer). Complete structure capped with silicon nitride layer is shown in Fig. 1. Before measurements the samples were exposed to atmosphere. The samples were subsequently treated at high temperature (HT), about 600 °C for 10 min in Ar to obtain uniform metastable phase of the composite films [13]. The thickness of each film of the multilayered structure was specified recently by Ciosek et al. [13] using of transition electron microscopy technique (TEM). The TEM image of a cross section of the structure (as deposited) shows reproducible ultra-thin (about 1.8 nm thick) Si films between Ti layers. The thickness of the formed layers was also evaluated by the sputtering rate and the depth of the final craters (stopping the sputtering at the multilayer/Si-substrate interfaces) after SIMS analysis using a Tencor α-step 100 profilometer. The sputter time into depth conversion is not trivial in the thin multilayer films. In view of the fact that different sputter rates for different matrices are present (its lower for Si in comparison to Ti material), the depth calibration should be done by stopping the sputtering at various interfaces. Such procedure can lead to overestimation of sputter rate and the corresponding thickness, when not steady sputtering conditions in the Si films are present (ultra-thin films). Additionally other aspects as atomic mixing, contaminations incorporated into the structure as well as charging effects should also be taken into the consideration in depth evaluation as they can alter the sputtering rate. Thus, the evaluation of each film thickness in the study was based on TEM cross section image of the structure and final crater depth measured using Tencor profilometer. More parameters of the fabricated structures are presented elsewhere [13].

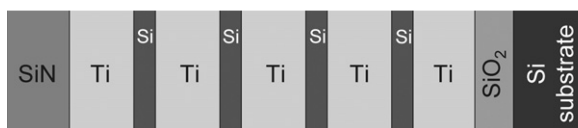

Fig. 1. Schematic structure of Ti/Si multilayer system created on Si-substrate and capped with SiN layer.

Our experiments were conducted using an SAJW-05 instrument, on which the mass spectrometer is Balzers QMA-410 quadrupole-based. The apparatus is also equipped with Physical Electronics ion gun with Ar^+ primary beam of about 100 μm in diameter. A 5 keV energy ion bombardment at 500 nA of beam current, rastered over 2000 μm × 3000 μm area, was used to obtain a low sputter rate and high secondary signal during sputtering.

3. Results and discussion

Here in the study we present Ar^+ SIMS depth profiling of Ti/Si multilayers. The SIMS profiles represented by distribution of positive atomic species (Ti^+, Si^+, C^+) and negative (O^-) of two Ti/Si multilayers (before and after the HT process) are plotted against sputter time in Fig. 2. The samples before and after annealing reveal quite different elemental distribution what is displayed by different sputter rate of the structures (when the final crater depths of both multilayers evaluated by Tencor are comparable). The periodicity of bilayer films are

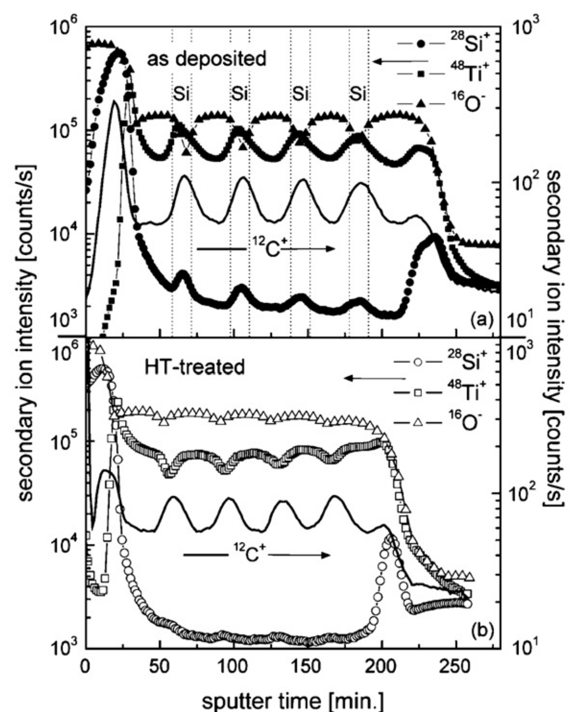

Fig. 2. SIMS depth profiles of atomic species taken with 5 keV Ar^+ beam for SiN/(Ti/Si multilayers)/Si as deposited (a) and after HT-treatment (b). Interface borders on Si-based films are indicated for as deposited structure. Each interface location has been established at 50% variation of Si^+ and/or Ti^+ (measured in linear scale).

fairly reproducible to a large degree in as deposited structure and partial intermixing of the Ti and Si layers is evident after annealing. High temperature treatment (Fig. 2b) leads to a more uniform distribution of Si as well as Ti in the multilayers indicating the beginning of titanium silicide formation. Wee et al. [14] have observed uniform distribution of $TiSi^+$ SIMS profile in Ti/Si treated at 620 °C for 60 min in the presence of oxygen. However, Capio et al. [15] postulate initial reaction between Ti and Si annealed at 600 °C for 30 min and that stable $TiSi_2$ phases are formed at temperatures ≥800 °C. XPS results obtained by Thian [16] for Ti/Si annealed at 620 °C for 100 min reveal a mixture of amorphous silicides and C49-$TiSi_2$ formation.

Here we will focus on depth profiling of Ti/Si multilayered structure annealed at 600 °C for 10 min and its counterpart (as deposited). The interesting data have been provided by the measurements of oxygen and carbon (Fig. 2) which exhibit high level of contamination in fabricated structures. The Ti–Si–O films are affected by water absorption when they are exposed to air after the fabrication process and an increase of impurities content (H, O) could be observed [17]. Also higher ion intensity of carbon is detected in the silicon-based films, while Ti-films reveal higher ion signal of oxygen. This characteristic would be effective on increased emission from electropositive titanium (matrix effects). In that case higher emission of Ti one should observe during sputtering of Ti-based matrix richer in oxygen. This relation is ambiguous when $^{48}Ti^+$ ion signal does not reflect expected distribution of titanium in the structure (see Fig. 2a). Namely, $^{48}Ti^+$ signal is higher in Si-based film (lower O signal) than in Ti-based matrix (higher O signal). We claim that the increase of Ti^+ in silicon layers does not represent a "real" distribution of titanium in examined structure. We declare also that Ti^+ intensity measured in Ti-based matrix is affected by oxygen presence (matrix effects)—lower values of Ti^+ ion intensity are expected with the absence of oxygen there. However, the sputtering efficiency of $^{48}Ti^+$ in Si-based thin films (some minor Ti content is expected in Si-based films due to intermixing process, but much lower than in Ti-matrix) is dominated by some other contaminations. Also ion mass interferences (e.g., Si-containing) could have an effect on Ti sputtering even though similar observation has been noticed for all other titanium isotopes $^{46–50}Ti$ as well as for Ti_2^+ and TiO^+ (these profiles are not shown). Influence of other factors (e.g., interface effects—not steady condition of sputtering, atomic mixing, surface roughness) are also not excluded when talking about anomalous behavior of Ti^+ distribution in the Ti/Si multilayers. We will return to that point later now noting only that in our opinion the most promising factor responsible for increased $^{48}Ti^+$ in Si-based films are contaminations incorporated into the structure. The Ti profile in Fig. 2b (annealed sample) is not governed by such characteristic indicating substantial changes of the multilayered matrix during high temperature treatment, what leads to different sputtering condition (e.g., for titanium). Thus, we conclude that the matrix effects of Ti are reduced significantly relative to the as deposited sample or ion mass interferences that take place in Si-based films are reduced in consequence of contaminations redistribution between layers after annealing. Also high signal of Ti^+ was monitored inside the SiO_2 rich layer and by the interfaces SiN/Ti and with Si-substrate due to oxygen-induced matrix effects. Higher concentrations of O are expected in the interface regions and in the SiO_2 rich layer in comparison to Si and Ti-based films. Thus, more productive emission of Ti^+ is reached in these regions (Figs. 2 and 3). Similar behavior is observed for Si^+ ion intensity registered during sputtering the cap film or the multilayer/substrate interface region related to the signal coming from Si-substrate. Depth profile of C after annealing presents insignificantly reduced signal and it still remains higher in Si than in Ti layers after HT-treatment. The last carbon peak seams to be broader in comparison to the other and falls into the Ti layer as a result of either initial deposition route or the effects of mixing during SIMS analysis. The depth resolution (depth interval over which the intensity variation falls from 84 to 16% of the maximum signal at interface) measured at the falling edge of Ti^+ profile at multilayer/substrate interface and amounts to about 5 nm. In order to reduce atomic mixing during sputtering and thus increase the depth resolution ultra-low primary ion energy (below 1 keV) should be applied in depth profiling of such thin films. However, the ultra-low energy bom-

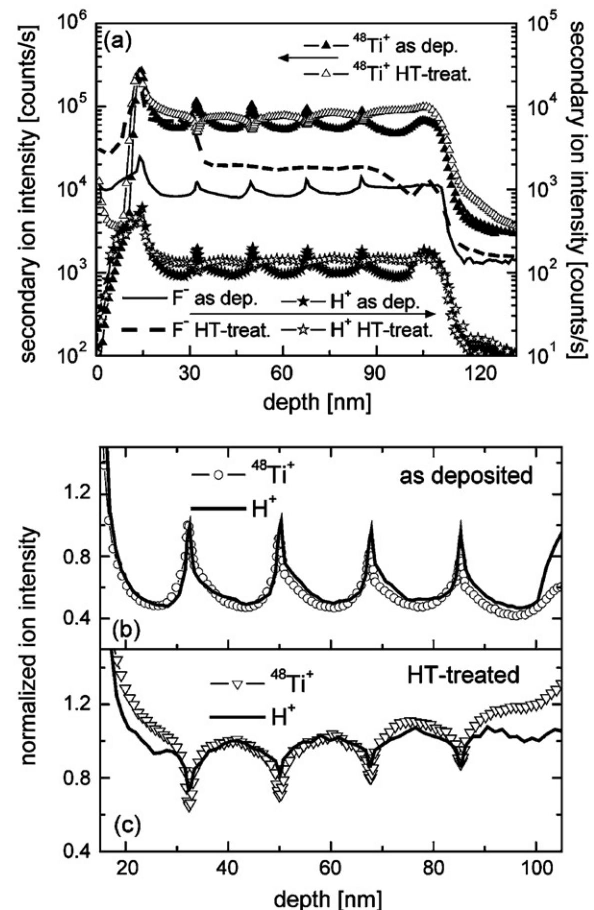

Fig. 3. (a) Hydrogen (the intensity values of H^+ were divided per 10) and fluorine distribution in comparison to Ti^+ signal of SiN/(Ti/Si multilayers)/Si before annealing (full symbols) and after HT-process (open symbols). Hydrogen profiles (lines) in relation to titanium distribution (symbols) in Ti/Si multilayers as deposited (b) and after HT-treatment (c).

bardment decreases the sputtering rate as well as sensitivity due to lower primary beam current particularly for molecular species detection.

We have also studied hydrogen and fluorine distribution in the multilayers (Fig. 3a). We observe one characteristic feature for both structures: the shapes of hydrogen and titanium profiles are exactly the same, only the intensities are different. Furthermore, a high signal of fluorine in both samples was noticed, however about two times higher ion signal of F was recorded in the sample treated at 600 °C, beside the SiN/Ti interface and adjoining Ti layer where F signal increases an order of magnitude after HT-treatment. Also fluorine distribution has a certain similarity to hydrogen profile shape in as deposited sample indicating that some ion mass interferences (as e.g., $^{19}(OH_3)^-$) would have an effect on $^{19}F^-$ detection, when X-ray photoelectron spectroscopy (XPS) study do not show any presence of fluorine in the investigated multilayers. However, SIMS technique has the advantage that is very sensitive and even trace amounts of F could be detected that confirms some fluorine incorporation into the samples during deposition process or after storing the samples in air.

In Fig. 3b and c normalized Ti^+ and H^+ intensities in linear scale are presented. The relative variations of H and Ti signals up and down from layer to layer imply that Si layers are contaminated with H and reversed after high temperature process, Si is redistributed and H signal is reduces in Si-based films. The feature of similar H^+ and Ti^+ profiles recorded in the Ti/Si multilayers could be associated either with various ion mass interferences containing H (e.g., $^{28–30}SiC_xO_yH_z$, where x, y and z denote number of atoms) or with matrix effects caused by hydrogen. In the first case, signal shape of molecular $^{28–30}SiC_xO_yH_z$ ion is dominated by H^+ intensity distribution. If the second hypothesis is assumed than hydrogen is responsible for matrix effects in SIMS depth profiling of Ti/Si multilayers in which the sputtered ion yields of $^{46–50}Ti^+$ (and also Ti_2^+ and TiO^+) depend strongly on the matrix chemistry (the yields increase with H signal in the film). Opposite behavior (Ti signal increases, while H decreases) is observed only in the last Ti layer and by the interface Ti/SiO_2 (HT-treated sample; Fig. 3a and c) since matrix effects caused by oxygen (or fluorine) predominate over effects that proposed and associated with H. Analysis of hydrogen implants into pure Ti bulk should be considered to confirm (or to exclude) the impact related to either H-induced matrix effects or H-containing ion mass interferences on the Ti^+ secondary ion yield. We do not exclude influence of other contaminations (in the form of ion mass interferences) on Ti and Si detection as that composed of N or Fe (common contaminations of Ti-targets) however N^+ and $^{56}Fe^+$ ions have the same weight as Si^{2+} and Si_2^+, respectively. In ref. [11] depth profiling of Ti/Si layers with varying O content shows that numerous mass interferences of the detected molecule $CsSi^+$ with Ti_3O^+ and $CsCO^+$ occur and lead to quantification errors.

The results recorded in sample before annealing (Figs. 2a and 3) suggest that Si layers are contaminated with hydrogen and also carbon which can originated either from the sputtered targets or during exposing them in air after the fabrication process. We do not exclude contaminants incorporation into the multilayer structures in both ways, however higher contents of H, C, O (and also N and Fe) are expected in Ti-based films since Ti target easily incorporates impurities and thus reliable source of higher ion signals of H^+ and C^+ measured in Si-based layers are matrix effects, intermixing or diffusion processes. After HT-treatment the redistribution of hydrogen is evident and H presence seems to be substantially reduced in Si layers and finally higher H^+ signal is recorded in Ti-based layers (Fig. 3).

We conclude that, here in Ti/Si superlattice the sputtering and ionization processes of titanium and silicon are complex issue due to contaminants. Thus, in order to determine depth profiles of Ti/Si multilayers, with significantly reduced effects of matrix and ion mass interferences, we propose to accomplish negative SIMS by recording of sputtered TiO_2^- and Si_2^- ions. Molecular ions can sometimes give real elemental depth distribution and lesser matrix effects than atomic species [18] as it is also in our case, where TiO_2^- and Si_2^- are relatively matrix insensitive and represent more probable distribution of titanium and silicon in the multilayers, respectively. Negative SIMS signal variations of O^- together with SiO_2^- and also TiO_2^- with Si_2^- (the last one is shown only for as deposited sample to make other profiles easier to follow) are presented in Fig. 4. In view of the fact that ion intensity of O^- increases after HT-treatment, higher emission of SiO_2^- (or Si^+ and Si_2^-) should be observed

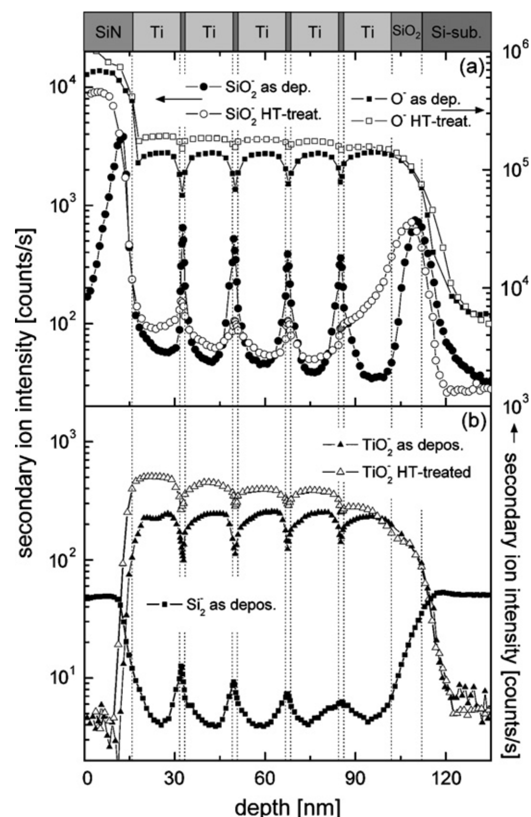

Fig. 4. Negative SIMS depth profiling with detection of (a) O^-, SiO_2^- and (b) molecular: TiO_2^- and Si_2^- ions of the multilayers as deposited (full symbols) and after HT-treatment (open symbols). The schematic structure of the Ti/Si multilayered system is shown above. The interfaces between the layers are indicated.

due to matrix effects, but here lower signal of SiO_2^- is detected indicating that interdiffusion processes of Si into Ti layers (and reversed Ti into Si-based films) are taking place and formation of Ti-silicide is observed. The SiO_2^- signal differs from the relation only in Ti layer adjoining the SiO_2 film probably due to stronger oxygen-induced matrix effects. Also TiO_2^- in the region differs from signals coming from other Ti layers and decreases with sputter time (depth) indicating changes of the structure and reduced content of Ti after annealing. Opposite trend reveals Ti^+ signal presented in Fig. 2 as reinforces our point of view that Ti^+ distribution is not real and more realistic concentration of Ti should be derived from TiO_2^- to avoid artifacts caused by contaminats. However, the methodology cannot be applied to Ti/Si multilayer in the lack of contaminations (e.g., oxygen). In conclusion we can say that negative molecular TiO_2^- and Si_2^- ion profiles present more realistic Ti and Si distribution (respectively) in the investigated structures as Fig. 4b indicates. Matrix effects caused by oxygen in SiN and by multilayer/substrate interface are significantly reduced and the highest value of Si_2^- intensity is measured in Si-substrate. Depth profile of Si_2^- after annealing (not shown) is quite similar as before annealing. The only difference relies on more uniform Si distribution in the Ti/Si regions as Si^+ shows in Fig. 2b. Profiles based on TiO_2^- in both samples (before and after annealing) provide lesser matrix effects and depict realistic distribution of Ti in the investigated multilayer films. Although the molecular ion detection do not remove these effects completely when much higher signal of TiO_2^- is measured in sample after HT-treatment.

It is worthwhile also to point out that the depth profile of the capping layer is affected by, characteristic for insulating material, a factor limiting the secondary ion emission induced by sample charging due to charged ion beam bombarding. This effect was observed previously by us in depth profiling of Si-oxide films with thickness higher than about 30 nm [19]. Here we have observed similar relation during SiO_2^- (Fig. 4a) and Si^+ or C^+ (Fig. 2a) registering. One important conclusion emerges from these results. Ability of SiN layer to oxidize results in insulating oxide formation and depth profile analysis without compensation treatment of this film is affected by charge build-up effect during ion beam bombarding. In addition charging effects alter the sputtering rate (and also ion signal values) in SiN layer resulting in overestimation of the thickness layer. Thus, initial measurements of all elements in the top layers are not very meaningful.

4. Conclusions

In conclusion, we can say that SIMS is an essential tool for depth profiling of thin multilayered films and for characterization of impurities (including hydrogen, carbon, oxygen and fluorine). We must emphasize also that negative mode of SIMS exhibits the superiority of molecular ions due to reducing the matrix effects over the positive atomic species for depth profiling of Ti/Si multilayers. Final conclusion from the study is, that the real distribution of titanium and silicon in Ti/Si multilayered superlattice should be derived from TiO_2^- and Si_2^- profiles which eliminate measuring artifacts due to matrix effects and ion mass interferences caused by contaminations embedded into the multilayer structures. Depth profile characterization with high depth resolution opens up possibilities for future design of superior Ti/Si nanostructures for optoelectronic application.

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