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Effect of a titanium cap in reducing interfacial oxides in the formation of nickel silicide

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Interfacial silicon oxide present at the Ni–Si interface hampers the silicidation between Ni and Si. In this work we present findings of the interaction of a Ti cap layer on top of Ni to remove the interfacial native oxide and chemically grown silicon oxide at several annealing temperatures. It was found that at 500 °C, Ti diffuses through the Ni layer and segregates at the Ni/Si interface, which subsequently reduces the interfacial silicon oxide and enables nickel monosilicide (NiSi) formation at 600 °C. The thickness of the Ti cap layer was found to strongly influence the temperature of the onset of nickel silicidation. A thin Ti cap layer resulted in the onset temperature of nickel silicidation being the same as that without a Ti cap layer, whereas a thick Ti cap layer lowered the onset temperature of the nickel silicidation.
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I. INTRODUCTION

Self-aligned silicide (salicide) processing is widely used in complementary metal–oxide–semiconductor (CMOS) manufacturing to reduce the sheet resistance and contact resistance of gate polysilicon and diffusion areas. Currently, the most commonly used self-aligned silicides are $TiSi_2$ and $CoSi_2$. For $TiSi_2$, the transformation from high resistivity C49 phase (60–90 $\mu\Omega$ cm) to low resistivity C54 phase (12–15 $\mu\Omega$ cm) is nucleation limited, causing linewidth dependence of the sheet resistance for lines narrower than 0.35 μm.[1–4] For this reason, $CoSi_2$ is currently being used for advanced generation of CMOS devices. However, as the junction depth continues to decrease, the silicide thickness is being scaled down to correspond to the lower amount of silicon consumption at the expense of higher sheet resistance. A new set of problems arises. These include the sensitivity of cobalt silicidation to interfacial surface cleanliness, ambient contamination, wafer degassing, and the inability (unlike Ti) of Co to reduce SiO_2.[5,6] Furthermore, the obtainment of epitaxial $CoSi_2$ has been limited by the formation of intermediate phases (primarily Co_2Si and CoSi), but has been shown to be achievable using additional techniques such as high temperature sputtering,[7] Ti interlayer mediated epitaxy (TIME),[8–12] oxide mediated epitaxy (OME),[13,14] and low temperature chemical vapor deposition (CVD) of cobalt.[15] Hence, NiSi is being investigated as a potential candidate for future device technologies because the same sheet resistance can be obtained with less Si consumption compared to $CoSi_2$.[16] Also, the low temperature range of 400–700 °C for NiSi stability not only makes NiSi compatible with ultrashallow junction CMOS devices but also means only a single annealing step is required (compared with two for the formation of C54-$TiSi_2$ and $CoSi_2$) in process integration of CMOS devices. However, the formation of NiSi is also extremely sensitive to interfacial native oxide contamination on the silicon surface. It has been reported that native oxide of about 20 Å on the Si surface is sufficient to retard any reaction between Ni and Si up to 800 °C. Therefore, humidity in the clean room environment and a time lag after the dilute HF clean prior to Ni deposition are important factors to consider for NiSi process integration.[17,18]

Recent studies of silicidation have shown that a Ti cap layer prevents oxygen adsorption on the as-deposited Co film. In this process, an epitaxial $CoSi_2$ film can be obtained.[19] It was further found that, due to its reactive nature, Ti is capable of gettering oxygen that is incorporated into the deposited metal and reducing interfacial oxide. Oxygen contamination during silicidation may originate from the following different sources: (1) the annealing ambient; (2) oxygen incorporated within the deposited metal layer; and (3) interfacial oxide at the metal/silicon interface.[20] Other advantages of a Ti cap include increased uniformity and thermal stability.[13] Studies of the effect of a Ti cap on the for-

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mation of NiSi have shown significant reductions in the junction leakage current.[21] The mechanism suggested is the suppression by Ti of the oxidation effect between the Ni silicide and the silicon interface. In this work, we study the effect of the Ti cap in removing interfacial oxides at the Ni/Si interface so that NiSi formation can take place.

II. EXPERIMENT

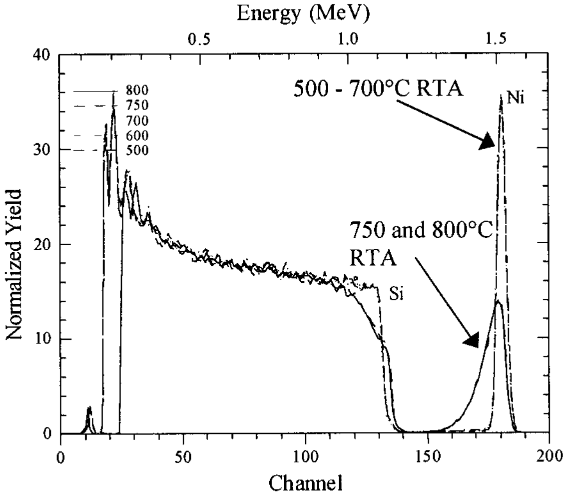
The substrates were *p*-type Si(100) wafers that were cleaned using the following sequence: SC-1 (a mixture of ammonium hydroxide, hydrogen peroxide, and water), followed by SC-2 (a mixture of hydrochloric acid, hydrogen peroxide, and water), each for 10 min at 60 °C, and finally by dilute hydrofluoric acid. Native oxide was then grown on the Si substrate by exposing the Si wafer to a clean room environment for one week. The thickness of the native oxide was measured to be about 16 Å (1.6 nm). Chemically grown silicon oxide (hereafter referred to as chemical oxide) was grown on the Si substrate by subjecting the Si wafer to SC-1 solution for 30 min at 60 °C in a spray processor. The thickness of the chemical oxide was measured to be 12–14 Å, which agreed with the value in the literature of about 12 Å.[22] Relative to native oxide, chemical oxide provides a well-controlled form of interfacial oxide for the present study. Nevertheless, native oxide realistically represents the type of silicon oxide that is present on the Si substrate upon exposure to the wafer fab or clean room environment. A film of Ni was deposited to a thickness of 30 nm on all the wafers using magnetron sputtering at a vacuum pressure of 8×10^{-3} Torr. Titanium films with thicknesses ranging from 5 to 15 nm were sputtered over the Ni film. After deposition, the films were subjected to rapid thermal annealing in nitrogen ambient for 1 min at various temperatures between 500 and 900 °C.

Phase identification was carried out using x-ray diffraction (XRD) and the interdiffusion between layers was studied by Rutherford backscattering spectrometry (RBS). The atomic redistribution and chemical identification were characterized by x-ray photoelectron spectroscopy (XPS) depth analysis and cross-sectional transmission electron spectroscopy (XTEM). The atomic ratio of the layers in XTEM was established by energy dispersive x-ray (EDAX) analysis.

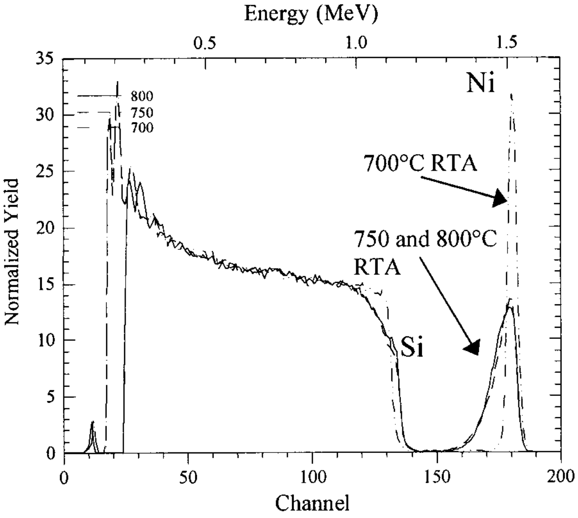
III. RESULTS

A. Without a Ti cap: Ni/interfacial oxide/Si

Figure 1(a) shows RBS spectra of a multilayered film stack consisting of 30 nm Ni/native oxide/Si after annealing at different temperatures. The Ni film remains unreacted up to a temperature of 700 °C as seen from the high Ni peak of narrow width at about 1.52 eV. Upon annealing at 750 and 800 °C, intermixing between Ni and Si was indicated by the transformation of the Si edge from a steep gradient to one of lesser gradient that extends toward the surface edge. The appearance of a shoulder near the Si interface at about 1.15 eV for these two annealing temperatures indicates silicide formation has taken place.[23] Phase identification by XRD, shown in Fig. 2, confirms the silicide to be epitaxial $NiSi_2$ at 800 °C rapid thermal annealing (RTA) whereas no silicide peak was observed for lower temperatures of 500–700 °C.



(a) Interfacial native oxide



(b) Interfacial chemical oxide

FIG. 1. RBS spectra for (a) Ni/native oxide/Si after RTA from 500 to 800 °C and (b) a Ni/chemical oxide/Si specimen after RTA from 700 to 800 °C.

The Ni/chemical oxide/Si sample shows similar results. As shown in Fig. 1(b), the RBS spectra indicate that silicidation commences only from 750 °C.

B. 10 nm Ti/Ni/interfacial oxide/Si (10 nm Ti capped Ni on native/chemical oxide)

Six 10 nm Ti capped Ni on chemical oxide samples were studied using XPS depth profiling (Fig. 3), RBS (Fig. 4), and XRD (Fig. 5). Figure 3(a) shows the XPS depth profiling of the first sample prior to RTA. It can be seen that both Ti and Ni have almost symmetric profiles. The intensity of the O signal decreases with depth but significantly rises to an atomic concentration of about 8% at a depth profiling time of about 1080 s. The latter observation infers the presence of chemical oxide at the Ni/Si interface and was supported by a Si 2*p* peak at 103.3 eV from a separate core XPS spectral analysis of a Si 2*p* nanoscan at that location. Further analysis

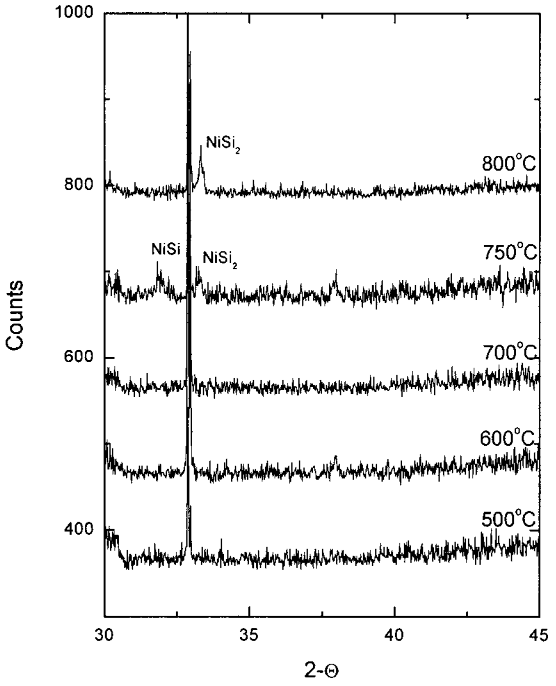


FIG. 2. XRD spectra of Ni/chemical oxide/Si after RTA from 500 to 800 °C.

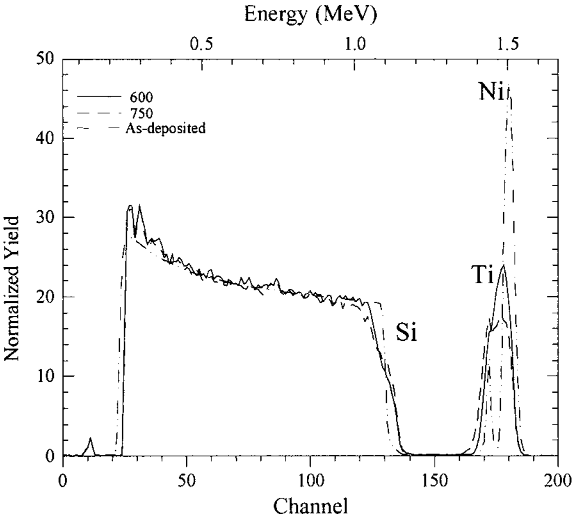


FIG. 4. RBS spectra of a 10 nm Ti/30 nm Ni/chemical oxide/Si sample prior to and after 600 and 750 °C RTA.

of the Ti 2p core XPS reveals the presence of oxidized Ti at the surface of the Ti cap layer, based on the Ti 2$p^{3/2}$ peak at 458.8 eV, indicating that the Ti may have reacted with ambient oxygen and formed TiO_2. In the Ni 2p XPS, the Ni 2$p^{3/2}$ peak at 852.8 eV is characteristic of metallic Ni.[23]

The second studied sample was the 10 nm Ti capped Ni on chemical oxide annealed at 500 °C. The XPS depth profiling analysis in Fig. 3(b) shows, interestingly, a significant amount of Ti in the upper and middle portions of the Ni film (depth profiling time of between 840 and 1320 s) and at the Ni/Si interface (depth profiling time of between 1320 and 1680 s). This observation infers diffusion of Ti from the cap layer through the unreacted Ni and subsequent accumulation at the Ni/Si interface. It is pertinent to remark that this Ti at the interface is not present in the as-deposited sample. Furthermore, there is a significant atomic concentration of O (about 8%) present at the Ni/Si interface (depth profiling time of about 1320 s). The XPS core spectra were examined,

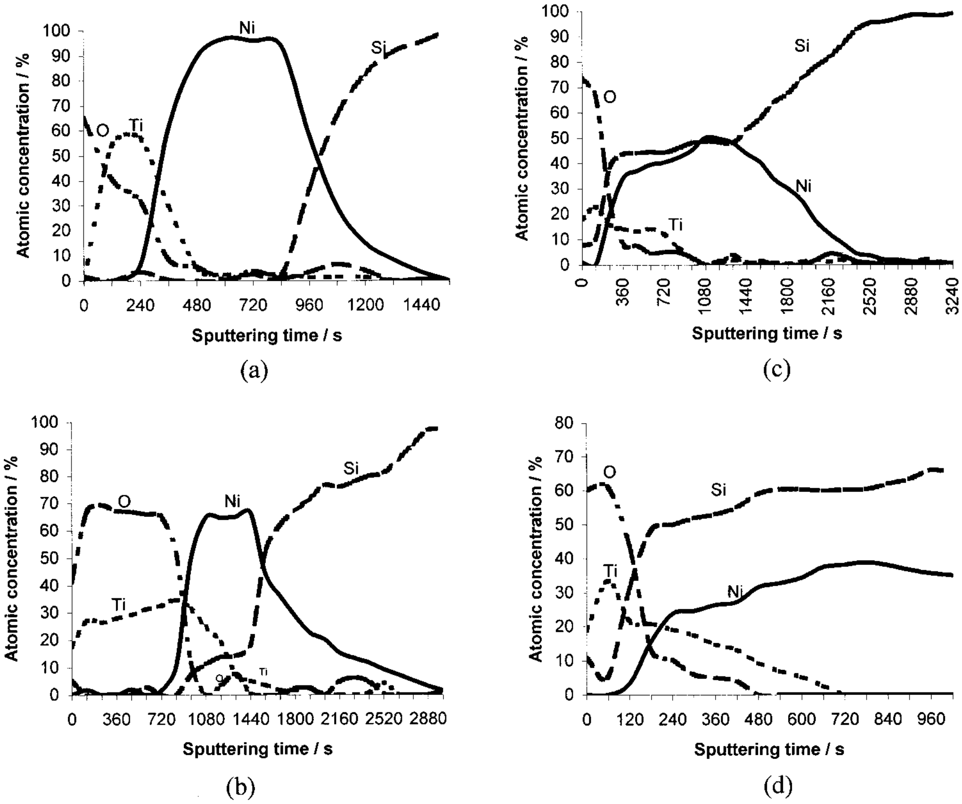


FIG. 3. XPS depth profiling of 10 nm Ti/30 nm Ni/chemical oxide/Si samples (a) as deposited and after RTA at (b) 500, (c) 600, and (d) 800 °C.

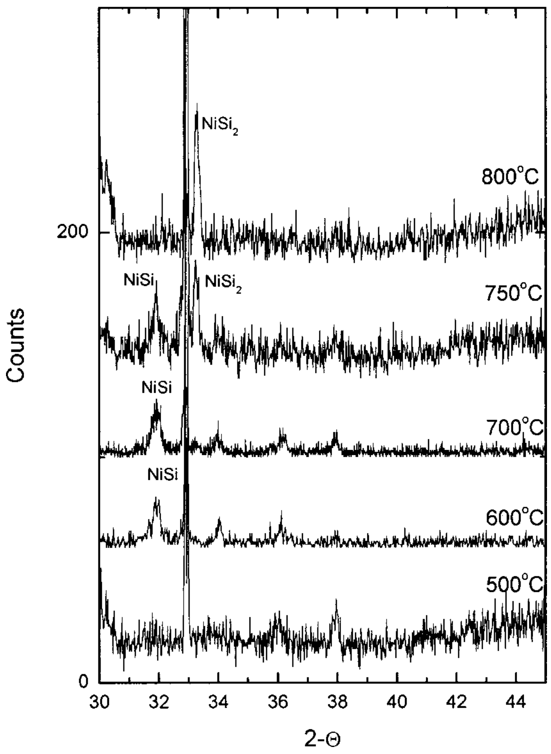


FIG. 5. XRD spectra of 10 nm Ti/30 nm Ni/chemical oxide/Si after RTA from 500 to 800 °C.

and the Ti 2p was analyzed at the following locations: (1) the surface of the Ti cap layer (depth profiling time of 0 s); (2) the Ti cap layer (240 and 720 s); (3) the Ti cap layer/Ni interface (960 s); (4) the middle of the Ni film (1200 s), and (5) the Ni/Si interface (1560 s). As shown in Fig. 6, it can be inferred that Ti occurs predominantly in an oxidized state on the surface of the Ti cap layer so the Ti 2$p^{3/2}$ peak at about 458.5 eV was attributed to likely be TiO_2.[24] The shoulder at about 458 eV adjacent to the TiO_2 peak in the Ti cap layer suggests the presence of another form of oxidized Ti. Interestingly, the shoulder subsequently becomes pronounced as part of a broad peak that includes elemental Ti (~455 eV). Since the Ti 2$p^{3/2}$ peak at 458 eV is absent in the as-deposited sample, its origin is probably due to the reaction between Ti and oxygen, resulting in the formation of titanium oxide other than TiO_2 (e.g., TiO). Similar observations of titanium oxides in Ti cap layers during cobalt silicide formation have been reported notwithstanding the performance of annealing in nitrogen ambient.[19]

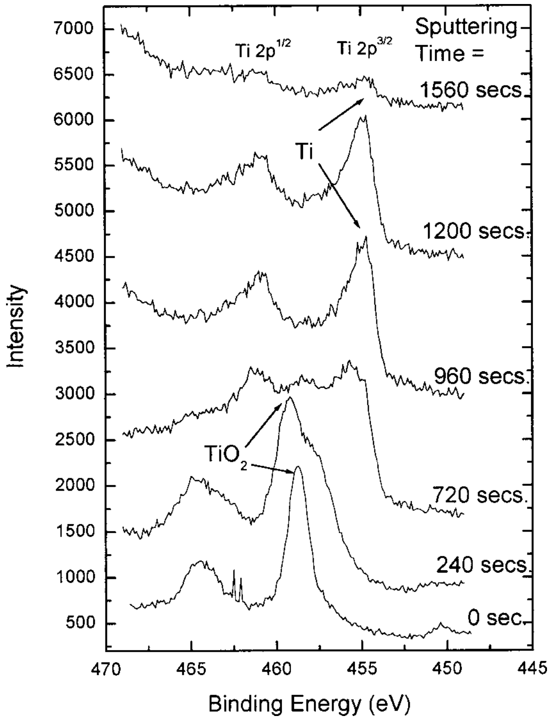
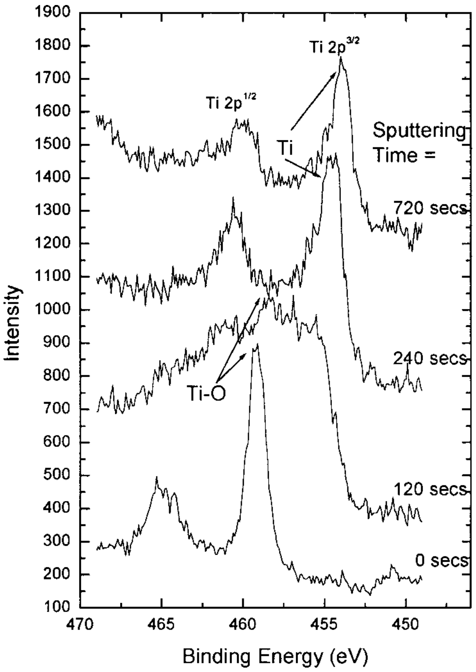


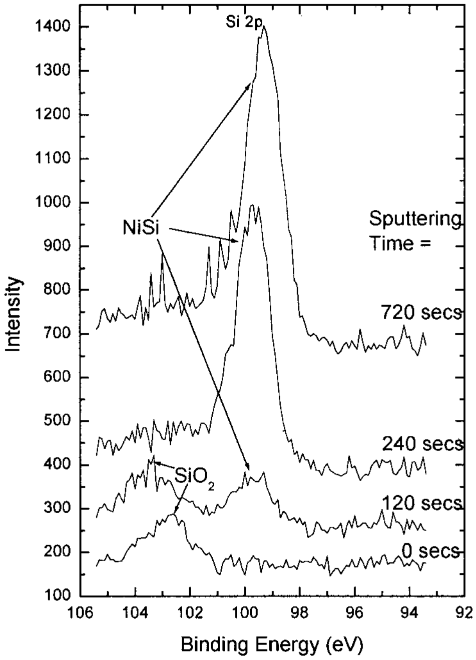
FIG. 6. Ti 2p XPS spectra of 10 nm Ti/30 nm Ni/chemical oxide/Si after 500 °C RTA at depth profiling times of 0, 240, 720, 960, 1200, and 1560 s.

At both the Ti/Ni and the Ni/Si interfaces, the Ti 2$p^{3/2}$ and 2$p^{1/2}$ peaks seen were attributed to elemental Ti, in agreement with another report.[19] For the Si 2p spectra (not shown), elemental or metallic Si was detected at the middle of the Ni film, at the Ni/Si interface, and in the Si substrate. Additionally, the analysis of the Si 2p spectrum taken after 1320 s of sputtering reveals the presence of elemental Si as well as oxidized Si. This infers that the chemical oxide is still present at the Ni/Si interface and thus implies that the reaction of the accumulated Ti with the interfacial chemical oxide has not yet begun at 500 °C. The XPS depth profiling [Fig. 3(b)] further shows the absence of NiSi formation since a consistent Ni:Si atomic ratio or intensity ratio was not observed. However, relative to the as-deposited sample [Fig. 3(a)], there appears to be an increased amount of intermixing between Ni and Si as well as an increase in the O:Ti atomic ratio or intensity ratio.

The third sample was the 10 nm Ti capped Ni on chemical oxide annealed at 600 °C. From the XPS depth profiling in Fig. 3(c), the observation of a consistent atomic concentration ratio or intensity ratio of Ni:Si (close to 1:1) infers that nickel monosilicide (NiSi) has formed. This finding is supported by the following: first, by the Ni 2$p^{3/2}$ peak at 853.5 eV in a separate core XPS analysis (not shown); second, by the NiSi peak present in the XRD (Fig. 5); third, by the intermixing of the Ni and Si inferred from the RBS spectra (Fig. 4). Further, in Fig. 3(c), although the intensity of Ti decreases as the multilayer film is sputtered away, there is nonetheless a significant amount (about 15 at. % or less) of Ti present in the surface portion of the NiSi layer. In fact, the intermixing of Ti and Ni can be seen from the RBS spectrum in Fig. 4 wherein the previously separated Ni and Ti edges (seen in the as-deposited sample) are now so close that the signals overlap. Core Ti 2p and Si 2p spectra (shown in Fig. 7) were analyzed at sputtering time of 0 s (surface of the Ti cap layer), 120 s (Ti cap layer), 240 s (Ti cap layer/NiSi interface), and 720 s (NiSi region). From Fig. 7(a), the presence of oxidized Ti (most likely TiO_2) was found at the Ti cap's surface, followed by a mixture of Ti compounds in the Ti cap layer as indicated by the broad peak (centered at about 457.5 eV), and last, elemental Ti in the bulk NiSi region. Similar to the sample that underwent RTA at 500 °C, the broad Ti 2$p^{3/2}$ peak comprises elemental Ti (~455 eV) and titanium oxide (~457.5 eV). Interestingly, in the Si 2p spectra [Fig. 7(b)], the presence of oxidized Si was detected at



(a) Ti 2p



(b) Si 2p

FIG. 7. (a) Ti $2p$ XPS spectra of 10 nm Ti/30 nm Ni/chemical oxide/Si after 600 °C RTA at depth profiling times of 0, 120, 240, and 720 s and (b) Si $2p$ XPS spectra of the same sample after 600 °C RTA at depth profiling times of 0, 120, 240, and 720 s.

the Ti cap's surface by virtue of the Si $2p$ peak at about 103.3 eV. Oxidized Si was also present in the Ti cap layer, but was accompanied by a second Si $2p$ peak at 99.5 eV. With regard to Si $2p$ in the bulk NiSi region, the Si $2p$ at 99.5 eV was attributed to oxidized Si resulting from NiSi formation. Support for the absence of titanium silicide formation was obtained from the absence of a $TiSi_2$ peak in the XRD data. Collectively, the aforementioned observations for the 600 °C annealed sample suggest the possible presence of ternary compounds comprising Ti, Ni, Si, and O in addition to titanium oxides and NiSi; this will be further addressed below for the Ti capped Ni on native oxide samples.

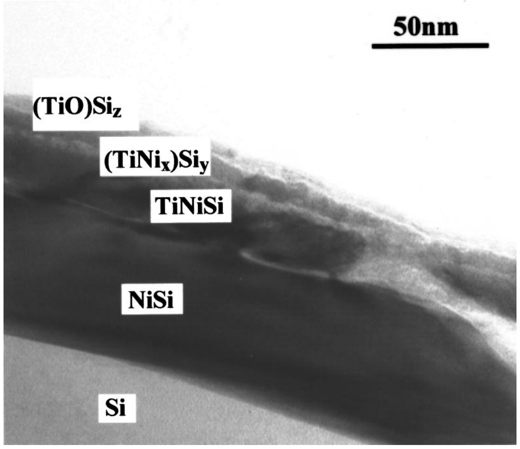


FIG. 8. XTEM image of 10 nm Ti/30 nm Ni/native oxide/Si after 600 °C RTA.

For the Ti capped Ni on chemical oxide sample annealed at 700 °C, it is pertinent to remark that the XRD and XPS depth profiling results are similar to those of the sample that underwent annealing at 600 °C. The next sample was one that was annealed at 750 °C. From the XRD data in Fig. 5, a peak attributed to $NiSi_2$ is now detected in addition to the NiSi peak. The RBS profile (Fig. 4) shows evidence of increased intermixing between Ni and Si compared to in the sample annealed at 600 °C.

The sixth sample studied was 10 nm Ti capped Ni on chemical oxide annealed at 800 °C. XRD [Fig. 3(a)] reveals the sole presence of $NiSi_2$. XPS depth analysis, shown in Fig. 3(d), depicts the presence of the cap layer, likely consisting of ternary compounds that comprises Ti, Ni, Si, and O, followed by the $NiSi_2$ layer incorporating Ti. The Ni $2p$ XPS core analysis confirms the presence of $NiSi_2$ from the Ni $2p^{3/2}$ peak position at 854 eV. Further analysis of the Ti $2p$ and Si $2p$ core spectra reveals the presence of oxidized Ti and oxidized Si (most likely Si–O) on the surface of the Ti cap layer as well as in the Ti cap layer, and elemental Ti and oxidized Si (99.5 eV corresponds to silicide in $NiSi_2$) in the bulk.

The behavior of the Ti capped Ni on native oxide samples (incorporating 10 nm of the Ti cap) seen in XRD, RBS, and XPS depth profiling spectra is similar to their chemical oxide counterparts. Indeed, the onset temperature for the formation of NiSi was significantly lowered to 600 °C. Moreover, like its chemical oxide counterpart, the significant presence of oxidized Ti, oxidized Si, in addition to elemental Ti and NiSi in the Ti cap layer suggests the possible presence of ternary compounds comprised Ti, Ni, Si, and O. A XTEM together with EDAX analysis was undertaken and is shown in Fig. 8, revealing that, besides the formation of the polycrystalline NiSi layer, there are also two ternary Ti–Ni–Si films [viz. $(TiNi_x)Si_y(x\sim0.2$ and $y\sim2)$ and TiNiSi] and a $(TiOSi_z)(z\sim0.2)$ layer above the NiSi layer.

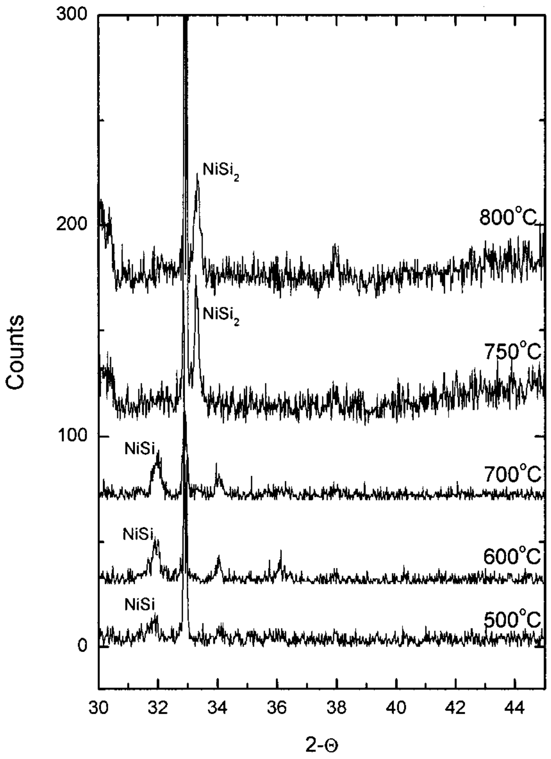


FIG. 9. XRD spectra of 15 nm Ti/30 nm Ni/native oxide/Si after RTA from 500 to 800 °C.

C. Varying the Ti thickness for Ti/Ni/interfacial oxide/Si

In order to study the effect of a thicker Ti cap layer on nickel silicidation, a 15 nm Ti cap was deposited over Ni. Figure 9 shows XRD scans for the 15 nm Ti capped Ni on native oxide after annealing between 500 and 800 °C. Interestingly, the NiSi peak was detected at 500 °C. For samples that were annealed from 600 to 800 °C, the phases of Ni silicides that formed are similar to the 10 nm Ti capped Ni on chemical or native oxide samples, with the exception that NiSi peaks were also found after annealing at 750 °C for the chemical oxide samples shown in Fig. 5. The XPS depth analysis in Fig. 10 infers NiSi formation at 500 °C by virtue of the consistent Ni:Si atomic ratio or intensity ratio (close to 1:1). Further core XPS analysis of the Ni 2p signal reveals the Ni 2$p^{3/2}$ peak position at 853.5 eV, which corresponds to that of NiSi. By comparing the present XPS depth profiling result with that of the 10 nm Ti capped Ni on chemical oxide sample annealed at 600 °C [Fig. 3(c)], two differing features can be observed. First, there is apparently more Ti in the Ti cap layer as indicated by the presence of a maximal atomic concentration of Ti at a depth profiling time of about 300 s. Second, the presence of Ni and Si falls short of reaching the surface of the Ti cap layer.

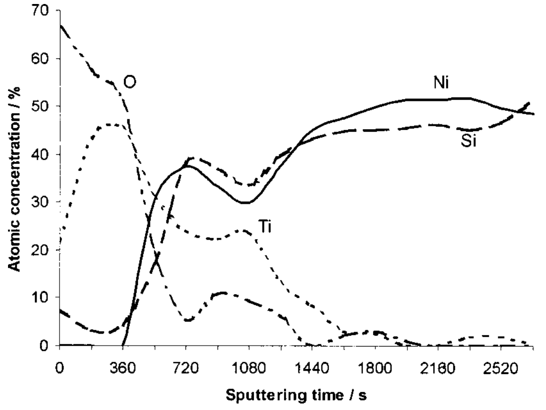
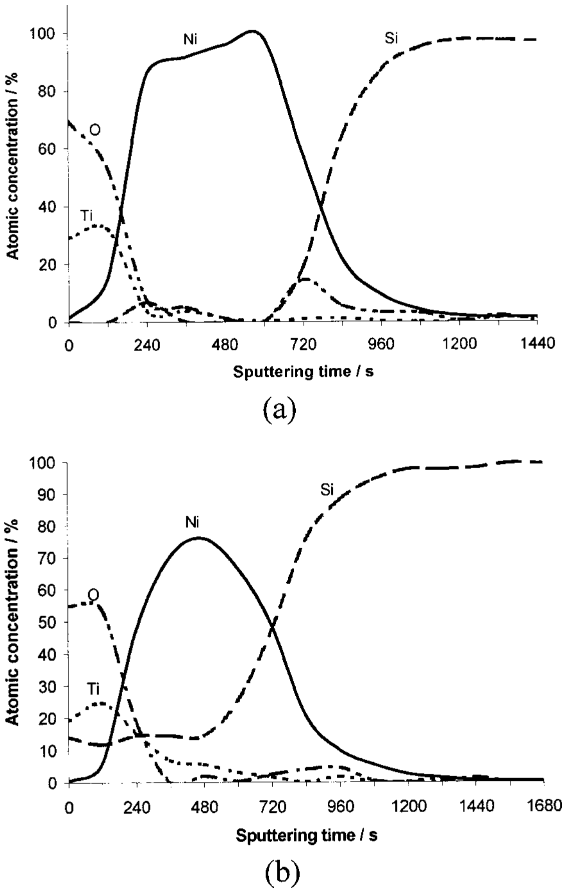


FIG. 10. XPS depth profiling of 15 nm Ti/30 nm Ni/native oxide oxide/Si after 500 °C RTA.



(a)

(b)

FIG. 11. XPS depth profiling of 5 nm Ti/30 nm Ni/chemical oxide/Si samples (a) as deposited and (b) after 700 °C RTA.

In contrast to its thicker Ti capped Ni counterpart, a thinner 5 nm Ti cap layer was found to be inefficient in reducing the silicidation temperature. Figure 11 shows the XPS depth profile of the 5 nm Ti capped Ni on chemical oxide prior to annealing (the as-deposited sample) and after annealing at 700 °C. The depth profile of the as-deposited profile for the present 5 nm Ti cap layer sample appears to be similar to that exhibited by the 10 nm Ti cap layer sample in Fig. 3(a), except that the Ti profile in the former is no longer symmetrical. Figure 11(b) shows the significant changes after annealing at 700 °C are the further diffusion of the Ti toward the bulk and the interdiffusion of Ni and Si. Upon closer examination, it can be seen that the Ti may not have reached the Ni/Si interface. Further XRD scans (not shown) confirm the absence of the formation of NiSi at 700 °C. In addition, RBS spectra of the 5 nm Ti/Ni/chemical oxide/Si sample (Fig. 12) reveal no drastic decrease in the height of

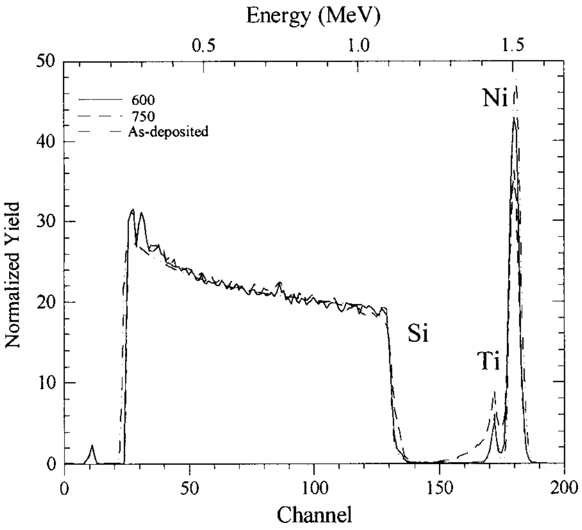


FIG. 12. RBS spectra of the 5 nm Ti/30 nm Ni/chemical oxide/Si sample prior to and after 600 and 750 °C RTA.

the Ni peak even up to a temperature of 750 °C. The spectrum of the sample after 750 °C annealing shows a small shoulder at the Si interface at about the 1.15 eV position, which indicates that intermixing has occurred. Unreacted Ni was inferred from a further experiment that involved sheet resistance measurements.

The aforementioned results for different thicknesses of Ti capped Ni on chemical oxide are also similarly observed for the samples that incorporate native oxide.

IV. DISCUSSION

A. Without a Ti cap: Ni/interfacial oxide/Si

With a standard dilute hydrofluoric acid dip to remove interfacial oxides prior to Ni deposition, polycrystalline NiSi formation occurs between 350 and 750 °C,[18] and this reaction is diffusion controlled.[25] The transition from NiSi to $NiSi_2$ is nucleation controlled and occurs at 750 °C.[26] Thus $NiSi_2$ is the stable phase at high temperatures. The presence of the native oxide layer serves as an effective kinetic diffusion barrier for the reaction between Ni and Si.[27] Therefore, at lower temperatures, Ni is unable to diffuse through the oxide to form NiSi. At higher temperatures, Ni could diffuse through probable defects like microchannels and pinholes in the native oxide, resulting in the formation of $NiSi_2$.[28,29]

By comparing the results associated with native oxide, it can be inferred that chemical oxide performs the same role as native oxide in inhibiting Ni diffusion into silicon at lower temperature, i.e., 500 °C. In the OME technique for epitaxial $CoSi_2$ growth,[13] chemical oxide was thought to function as a diffusion barrier which delayed the Co–Si reaction until the annealing temperature exceeded 500 °C, thereby inhibiting the formation of the intermediate Co_2Si and CoSi phases.[13] In the present study, the presence of epitaxial $NiSi_2$ and the nonobservance of NiSi is an indication that the chemical oxide may have suppressed the formation of intermediate NiSi during the formation of $NiSi_2$.

Nevertheless, the lack of evidence for NiSi in both chemical oxide and native oxide samples may not preclude the formation of NiSi because NiSi may have been initially formed during annealing but the rate of formation of NiS_2 is so favorable that conversion to $NiSi_2$ takes place after a very short time during high temperature annealing, such as at 800 °C.[17]

B. Ti/Ni/interfacial oxide/Si

By putting together the results of RBS, XRD, XPS depth analysis, and TEM, a possible reaction mechanism can be established for the 10 nm Ti capped Ni samples. Prior to annealing, the surface of the Ti cap was converted to a thin layer of TiO_2. During annealing at 500 °C, two significant events occur. First, the Ti cap layer undergoes further reaction with oxygen from the annealing ambient to form a mixture of TiO_2 (at the surface of the Ti cap layer) and probably TiO (beneath the surface). The formation of the latter mixture could also occur through a reaction with oxygen within the Ti cap layer on the assumption that the oxygen present is only loosely bonded to the Ti at the grain boundaries. Second, free Ti from the Ti cap layer diffuses into the Ni film, and accumulates at the Ni/Si interface. Annealing at 600 °C results in not only the formation of NiSi, but also the formation of ternary titanium–nickel–silicon compounds [TiNiSi and $(TiNi_x)Si_y$] and a $TiOSi_z$ layer. These ternary compounds were "pushed" toward the surface during NiSi formation.

A previous study has documented that, in a Ti/Co/SiO_2 system, the thin layer of Ti is able to diffuse through the Co to the Co/SiO_2 interface, whereafter Ti reduces the SiO_2.[30] The free energy change (ΔG) for the reaction: $Ti+SiO_2 \rightarrow TiO_2+Si$ is negative ($\Delta G_{1023\,K}=-34\,kJ/mol$),[31] which indicates that it is a favorable reaction. Thus, the driving force for the accumulation of the Ti at the Ni/native oxide and Ni/chemical oxide interfaces (interfacial segregation) appears to be related to the strong affinity of Ti to both interfacial silicon oxides.[30] From our study, the observation of NiSi formation at 600 °C is a strong indication that the accumulated Ti has reduced the chemical oxide or the native oxide to TiO_2 and free Si. The latter Ti oxide may then serve as a diffusion membrane whereby Ni can diffuse towards the Si substrate, resulting in the formation of NiSi. The XPS depth profiling analysis does not show a buildup of Ti oxide in the bulk because the native oxide is very thin (about 12 Å) and the Ti oxide formed as a result of the reduction could not be accurately characterized using XPS. In another study using a Ti/Co/SiO_x (chemical oxide) system, the Ti accumulated at the Co/Si interface reduced the chemical oxide to some form of $Co_xTi_yO_z$, whereupon at higher annealing temperatures, the Co diffused through the $Co_xTi_yO_z$ and reacted with the Si to form CoSi.[32] Interestingly, the presence of a $TiOSi_z$ layer from TEM in the present study appears to suggest an alternative mechanism wherein the accumulated Ti may have reacted with the native oxide or chemical oxide to form $TiOSi_z$. The latter ternary compound then acts as a diffusion membrane, and eventually gets "pushed" up to the surface during NiSi formation. The existence of $TiOSi_z$ can be supported by the absence of a Ti–SiO_2 tie line from the Ti–O–Si ternary phase diagram.[33] This mechanism receives further support from the detection of oxidized Ti (probably TiO) and oxidized Si (probably SiO) in the core Ti 2*p* and Si 2*p* XPS analysis of the Ti cap layer. Nevertheless, if the mechanism relates to reduction of the interfacial oxide to TiO_2, then the origin of silicon in the $TiOSi_z$ compound is probably due to the diffusion of silicon into the Ti cap layer during NiSi formation at 600 °C.[34]

Evidence of the formation of TiO_x or $TiOSi_z$ on top of TiNiSi/NiSi as a result of Ti gathering of Si–O native oxide/grown oxide is further confirmed by a separate experiment where an interlayer Ti was used to gather the oxide in the Ni/Ti/oxide/Si system.[35] In this particular system, after a 500 °C RTA, a layer of Ti oxide was detected on top of the TiNiSi/NiSi layer. A similar mechanism whereby the Ti oxide gets pushed up to the surface during the NiSi formation is postulated.

The structure of the ternary titanium–nickel–silicon compounds is presently unclear but the absence of $TiSi_2$ from the XRD and TEM results of the Ti capped samples at 600 °C indicates that the basic compound is nickel silicide. Titanium disilicide is not expected to form until about 650 °C. Interestingly, the nonobservation of titanium silicide even after annealing at 700 °C suggests *prima facie* that the reaction between nickel and silicon is kinetically faster than that between titanium and silicon, since Ti is also expected to competitively diffuse through the TiO_2 or $TiOSi_z$ diffusion membrane together with Ni. The heat of formation of Ni_2Si (−34 kcal/mole) is more negative than that for $TiSi_2$ (−30 kcal/mole).[36] Therefore, Ni_2Si forms more easily and it eventually fully converts to NiSi during the annealing process. Furthermore, the TEM micrograph in Fig. 8 also suggests that formation of the ternary phase is more favorable than formation of $TiSi_2$.

C. Variation of the Ti cap layer thickness

The aforementioned results suggest a dual function for the Ti cap layer: protection of the underlying nickel from oxygen contamination and reduction of the interfacial oxide thereby enabling the formation of NiSi. Furthermore, the present study shows evidence that the formation of NiSi is dependent on the thickness of the Ti cap layer. With regard to the silicidiation at 600 °C for the 10 nm Ti/Ni/interfacial oxide system, the onset temperature for silicidation was delayed until 750 °C when a thinner 5 nm Ti cap layer was used whereas the temperature decreased to 500 °C in the case of a thicker 15 nm Ti cap. The results in the present study are in agreement with another study that employed a Ti/Co/oxide wherein thin Ti cap layers (1–2 nm) resulted in a delay in the silicidation to CoSi phase to 700–800 °C while a thicker Ti cap lowered the temperature of CoSi formation to almost the normal value for direct Co/Si reaction without an interfacial oxide.[20] The thickness dependence can be explained in terms of the diffusion kinetics of Ti. Fick's equation[37] states that

$$F = -D\frac{\partial C(x,t)}{\partial x}$$

and

$$D = D_0 \exp(-E_a/kT).$$

Therefore, the concentration gradient and temperature are two important factors that affect a diffusion process. When the Ti cap layer is thicker, the concentration gradient can be maintained over a longer time, because there is sufficient Ti remaining in the Ti cap layer after some diffusion (nearly 100% Ti concentration at the surface) to drive the diffusion flux. For a thinner layer of Ti cap layer, once the Ti diffuses into the bulk, the concentration of Ti at the surface and in the subajacent region incorporating the Ni does not differ much. Even if the time allowed for diffusion of Ti in both the thicker and thinner Ti cap layers is the same, the diffusion gradient of the Ti in the thinner cap layer is insufficient to drive the diffusion flux. Thus, a higher temperature is required to drive the diffusion mechanism. It was shown that, with a 10 nm Ti cap, Ti could successfully diffuse through Ni and remove the native oxide or chemical oxide at 600 °C. A 15 nm Ti cap can do likewise but at lower temperature of 500 °C due to the reason stated above. When too thin (5 nm) a Ti layer is deposited as the cap layer, it becomes ineffective in lowering the silicidation reaction temperature. The formation sequence at each temperature behaves exactly like in the case in which no Ti cap was deposited. During annealing, there is not much Ti left to diffuse through Ni to remove interfacial oxide.

V. CONCLUSION

We have demonstrated the use of a Ti cap layer in removing interfacial oxides on the Si surface and in promoting a silicidation reaction between Ni and Si. Both native oxide and chemical oxide play the same role in hindering any reaction between Ni and Si up to 750 °C and they can be reduced by a Ti cap layer whereby Ti diffuses through Ni and reduces the oxide during silicidation. It was also demonstrated that a thicker Ti capping layer is able to reduce the onset temperature of NiSi in the presence of such interfacial oxides. However, if too thin a Ti cap is deposited, the Ti could react with the ambient oxygen and lead to an insufficient amount of Ti that is able to diffuse and take part in the reduction process. As a result, the Ti cap would be totally ineffective in lowering the silicidation temperature.

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[1] H. Jeon, C. A. Sukow, J. W. Honeycutt, G. A. Rozgonyi, and R. J. Nemanich, J. Appl. Phys. **71**, 4269 (1992).
[2] J. B. Lasky, J. S. Nakos, O. J. Cain, and P. J. Geiss, IEEE Trans. Electron Devices **ED-38**, 262 (1991).
[3] Z. Ma, L. H. Allen, and D. D. Allman, J. Appl. Phys. **77**, 4384 (1995).
[4] J. A. Kittl and Q. Z. Hong, Thin Solid Films **320**, 110 (1998).
[5] W. J. Freitas and J. W. Swat, J. Electrochem. Soc. **138**, 3067 (1991).
[6] K. Suguro *et al.*, Mater. Res. Soc. Symp. Proc. **514**, 171 (1998).

[7] K. Inoue, K. Mikagi, H. Abiko, and T. Kikkawa, Tech. Dig. - Int. Electron Devices Meet. , 445 (1995).

[8] S. L. Hsia, T. Y. Tan, P. Smith, and G. E. McGuire, J. Appl. Phys. **72**, 1864 (1992).

[9] A. Vantomme, M.-A. Nicolet, G. Bai, and D. B. Fraser, Appl. Phys. Lett. **62**, 243 (1992).

[10] S.-L. Zhang, J. Cardenas, F. M. d'Heurle, B. G. Svensson, and C. S. Petersson, Appl. Phys. Lett. **66**, 58 (1995).

[11] G. B. Kim, H. K. Baik, and S. M. Lee, Appl. Phys. Lett. **69**, 3498 (1996).

[12] S. Hong, P. Wetzel, G. Gewinner, and C. Pirri, J. Vac. Sci. Technol. A **14**, 3236 (1996).

[13] R. T. Tung and F. Schrey, Appl. Phys. Lett. **67**, 2164 (1995).

[14] S. Ohmi and R. T. Tung, Mater. Res. Soc. Symp. Proc. **564**, 117 (1999).

[15] A. R. Londergan, G. Nuesca, C. Goldberg, C. Peterson, A. E. Kaloyeros, B. Arkles, and J. J. Sullivan, J. Electrochem. Soc. **148**, C21 (2001).

[16] A. Lauwers *et al.*, Microelectron. Eng. **50**, 103 (2000).

[17] P. S. Lee, D. Mangelinck, K. L. Pey, J. Ding, J. Dai, C. S. Ho, and A. See, Microelectron. Eng. **51**, 583 (2000).

[18] X. W. Lin, N. Ibrahim, L. Topete, and D. Pramanik, Mater. Res. Soc. Symp. Proc. **514**, 179 (1998).

[19] G. B. Kim, J. S. Kwak, and H. B. Biak, J. Vac. Sci. Technol. B **17**, 162 (1999).

[20] C. Detavernier, R. L. Van Meirhaeghe, F. Cardon, R. A. Donaton, and K. Maex, Microelectron. Eng. **50**, 125 (2000).

[21] T.-H Hou and T.-F. Lei, IEEE Electron Device Lett. **20**, 572 (1999).

[22] T. Suzuki and S. Adachi, Jpn. J. Appl. Phys., Part 1 **33**, 2689 (1994).

[23] D. Manglinck, Y. J. Dai, J. S. Pan, and S. K. Lahiri, Appl. Phys. Lett. **75**, 1736 (1999).

[24] D. J. Cole and E. H. Phoderick, J. Phys. D **9**, 965 (1976).

[25] *Handbook of X-Ray Photoelectron Spectroscopy* (Physical Electronics, Perkin-Elmer, Eden Prairie, MN, 1995).

[26] F. M. d'Heurle, S. Petersson, L. Stolt, and B. Stritzker, J. Appl. Phys. **53**, 5678 (1982).

[27] P. S. Lee, D. Mangelinck, K. L. Pey, Z. X. Shen, J. Ding, T. Osipowicz, and A. See, Electrochem. Solid-State Lett. **3**, 153 (2000).

[28] H. Dallaporta, M. Liehr, and J. E. Lewis, Phys. Rev. B **41**, 5075 (1990).

[29] J. T. Mayer, R. F. Lin, and E. Garfunkel, Surf. Sci. **265**, 102 (1992).

[30] E. Kondoh, T. Conard, B. Brijis, S. Jin, H. Bender, M. de Potter, and K. Maex, J. Mater. Res. **14**, 4402 (1999).

[31] *CRC Handbook of Physics and Chemistry*, 64th ed. (Chemical Rubber, Boca Raton, FL, 1983).

[32] C. Detavernier, R. A. Donaton, K. Maex, S. Jin, H. Bender, R. V. Meirhaeghe, and F. Cardon, Mater. Res. Soc. Symp. Proc. **564**, 139 (1999).

[33] R. Beyers, J. Appl. Phys. **56**, 147 (1984).

[34] F. Fenske, A. Schopke, S. Schulze, and B. Selle, Appl. Surf. Sci. **104/105**, 218 (1996).

[35] W. L. Tan, K. L. Pey, S. Y. M. Chooi, and J. H. Ye, Mater. Res. Soc. Symp. Proc. (2001) (in press).

[36] *Properties of Metal Silicides*, edited by K. Maex and M. van Rossum INSPEC, London (1995), p. 55.

[37] *VLSI Technology*, 2nd ed., edited by S. M. Sze (McGraw–Hill, New York, 1988), p. 275.