In situ real-time studies of nickel silicide phase formation

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The formation of NiSi films on Si was studied using Rutherford backscattering spectrometry, atomic force microscopy, and ellipsometry. NiSi is an attractive candidate for use as a gate contact material due to its low metal-like resistivity and large processing window (350–750 °C). Three phases, Ni_2Si, NiSi, and $NiSi_2$, were identified in this temperature range, and their optical databases in the 2–4 eV photon range were established, and used to model real-time ellipsometry data. It is shown that real-time ellipsometry can be used to monitor and follow the formation of the various Ni–Si phases. We have also observed the onset of agglomeration of the silicide for longer time anneals at temperatures of 500–700 °C, which is much lower than 1000 °C where agglomeration has been reported to occur. © *2001 American Vacuum Society.* [DOI: 10.1116/1.1347046]

I. INTRODUCTION

Metal silicides continue to attract considerable attention as low resistivity metal contacts and interconnect materials in microelectronics.[1] As device size decreases, the amount of Si consumed in the course of the Si-metal reaction becomes a major issue, because low Si consumption is crucial to maintain shallow source and drain junctions.[1,2] Among the most desirable silicides are those that have low Si consumption, low metal-like resistivities, low processing temperatures, and high temperature stability. NiSi meets most of these criteria in that it has a low resistivity of 14 $\mu\Omega$ cm, a large formation temperature window of 350–750 °C,[3–6] and low Si consumption (0.82) in comparison to other commonly studied silicides such as $TiSi_2$ [1,7](0.9) and $CoSi_2$(1.04),[1,5] and NiSi does not require multistep processing to form the low resistivity silicide phase.[1,4,5]

In the Ni–Si phase diagram, there are three major phases, Ni_2Si, NiSi, and $NiSi_2$. It would be useful to have a method to selectively produce and detect the desired NiSi phase. It is the objective of this research to develop analytical procedures that enable the monitoring of phase transformations in real time using nondestructive *in situ* techniques, specifically, the formation of NiSi in real time. To this end, we investigate nickel silicide phase formation which results in the three nickel silicide phases (Ni_2Si, NiSi, $NiSi_2$), each having different properties, and each forms in different temperature ranges below 1000 °C. It has been reported that Ni_2Si, NiSi, and $NiSi_2$, form in the ranges 200–350, 350–750, and 750–1000 °C, respectively,[1–10] and at 1000 °C, agglomeration takes place where $NiSi_2$ loses adhesion to Si near the melting point of $NiSi_2$ (993 °C),[10] thereby forming clusters on the surface. In order to monitor the silicide formation process, specifically NiSi, we follow this phase transformation by studying the changes on the surface using real-time single wavelength ellipsometry (RTE) and spectroscopic ellipsometry (SE). Since previous studies of the optical properties of nickel silicides[8,9] are limited, we remeasured the optical properties of the three nickel silicide phases, and used these results as a database. Also, we use SE, in conjunction with Rutherford backscattering spectrometry (RBS), which provides compositional information at varying depths, to identify the phases, and the extent of phase formation for anneals at various temperatures and times. Samples were annealed for short and long times, in order to check for homogeneity of the phases formed, and to watch for changes on the surface that may result from prolonged annealing. We have observed that long time anneals can lead to the onset of agglomeration of the silicide phases, even at low temperatures where agglomeration is not expected. RTE results show the phase transformations in real time.

II. EXPERIMENT

Samples of 25 nm Ni films were electron-beam deposited onto (100) oriented single crystal Si. These samples were annealed for various times (2, 5, 10, 15, and 20 min) at several temperatures (550, 650, and 750 °C). The rapid thermal processing chamber used for these anneals was a custom built stainless steel, water cooled, turbo pumped system with a base pressure of $\sim 10^{-8}$ Torr, and is equipped with an *in situ* ellipsometer. Quartz iodine lamps heat the sample in the chamber through a fused silica window. This system is not capable of performing stable temperature anneals of less than 2 min. Therefore, samples annealed for 30 s at temperatures ranging from 175 to 1000 °C were done using a Heatpulse 8108 rapid thermal processing system,[1] at STEAG RTP Systems Inc. Some real-time studies were also conducted under nonrapid thermal conditions in a custom-built integrated ion beam sputter deposition system with *in situ* real-time SE capabilities.[11] Spectroscopic ellipsometry data were taken in the energy range of 2.2–4.1 eV at an incident angle of 70°, using a custom built *ex situ* ellipsometer. All the samples

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were annealed in vacuum, with a pressure of $\sim 10^{-8}$ Torr. Sample surfaces were imaged before and after the anneals using atomic force microscopy (AFM) to obtain mean and rms roughness values. The samples were also analyzed by RBS using a 2.3 MeV He^+ ion beam at a 60° tilt angle. RBS was used to measure elemental ratios of Ni:Si at varying depths. RUMP,[12] an RBS analysis and simulation program, was used to model the raw data (intensity versus channel numbers) to obtain thicknesses and composition of the films. X-ray photoelectron spectroscopy (XPS) was employed for phase identification at the sample surface.

SE is a sensitive, nondestructive, and a noninvasive optical technique that has been used extensively in Si processing technology both as an *ex situ* analytical tool, and as an *in situ* monitoring technique.[13,14] Ellipsometry can be used to measure the dielectric function (ϵ) for films and surfaces. ϵ is related to Ψ and Δ, the two measurables of ellipsometry that represent the change in amplitude and phase, respectively, of linearly polarized light as it interacts with the sample. The dielectric function is complex where the real part ϵ_1 is related to the refractive index, and the imaginary part ϵ_2 is proportional to the absorption coefficient. For ellipsometric modeling of inhomogeneous media, the Bruggeman effective medium approximation (BEMA)[15] was used, which assumes that for a mixed composition film each component can be represented by its bulk dielectric function, and each component is large relative to the wavelength of the probing radiation. Thus, using known optical properties in the BEMA, the ellipsometric data can be modeled to obtain the thickness and composition of the various silicide films that form during the annealing process.[15] The relative quality of the fit of ellipsometric data to a particular model is reported as the root mean square error (RMSE). The RMSE can be used to compare fits to one model.

III. RESULTS AND DISCUSSION

RBS and XPS were used to obtain compositional information about the 30 s annealed samples, and AFM for roughness information, all of which is necessary to construct ellipsometry models. Annealing a 25 nm thick Ni layer on Si will yield a 38 nm Ni_2Si, 55 nm NiSi, and a 70 nm thick $NiSi_2$ layer.[6] RBS should yield a 66:33, 50:50, and a 33:66 Ni:Si ratio for Ni_2Si, NiSi, and $NiSi_2$, respectively, based on stoichiometry. RBS measures elemental ratios and yields composition information with 1%–5% accuracy. Since the thickness of films calculated from these elemental ratios depend on the uniformity of film thicknesses, density of the phases, energy straggling, etc., a conservative estimate of error in thickness is assumed to be 10%. Here, the elemental ratios and film thicknesses are reported keeping the margins of error in mind. Backscattering spectra, shown in Fig. 1, for the 30 s anneals at 200 and 250 °C yield an approximately 37 nm thick surface layer with a 60:40 Ni:Si ratio. The 500 °C anneal yields a 50 nm thick layer with a 50:50 Ni:Si ratio, and the 800 °C anneal yields a 70 nm layer with a 30:70 Ni:Si ratio. Thus, based on the RBS results, these three sets of samples most likely represent the Ni_2Si, NiSi, and the $NiSi_2$ phases, respectively. These samples do show a slightly larger amount of Si at the surface than expected for pure silicide phases. XPS revealed the presence of SiO_2 (peak position at 103.3 eV) at the surface, which is known to readily form on silicide surfaces.[16] This would contribute to the Si content on the surface, and would explain the excess Si, as observed by RBS. XPS could not be used to distinguish between the different silicide phases since the binding energies of nickel (852.7 eV), silicon (99.3 eV), and their silicides (853.1–853.5, 98.4–99.9 eV),[17] were too close to be resolved by the XPS instrument that we used.

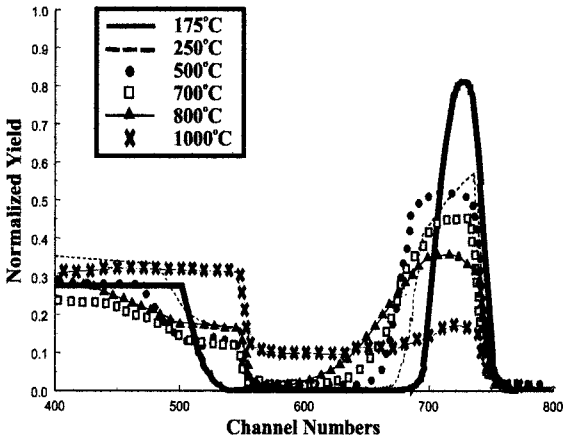

FIG. 1. RBS spectra for 30 s anneals at 175, 250, 500, 700, 800, and 1000 °C.

AFM roughness results for short (30 s) and long time anneals are shown in Figs. 2 and 3, respectively. For both anneals, a general trend of increasing mean and rms roughness, with increasing annealing temperature and time, is observed. Figure 2 shows that the 1000 °C anneal for 30 s, representing the agglomeration stage, produces a distinctly different looking surface with sharp needlelike structures and deep valleys. Figure 3, which shows the AFM images for samples annealed for longer times at 550, 650, and 750 °C, shows that longer time anneals at these temperatures, much lower than 1000 °C, also yield agglomerationlike surfaces with sharp needlelike structures, as was observed for the 30 s, 1000 °C anneal, that is known to show agglomeration.[3] Thus, it appears that agglomeration can occur even at lower temperatures, for long time anneals.

Figure 4 shows SE data (in terms of ϵ_1 and ϵ_2 versus wavelength) for samples annealed for 30 s at various temperatures. The ϵ data (Fig. 4), especially ϵ_2 spectra shown in Fig. 4(b), shows similar spectra paired and marked (1–4) for anneals at 175 and 200 °C (1), 250 and 400 °C (2), 500 and 600 °C (3), and 700 and 800 °C (4). From the formation temperatures, it is likely that three sets of spectra, marked (2), (3), and (4), represent the three nickel silicide phases, Ni_2Si, NiSi, and $NiSi_2$, respectively. The concordant SE and RBS data for the 30 s anneals at 250, 500, and 800 °C very likely represent Ni_2Si, NiSi, and $NiSi_2$, respectively, and thus the data from these samples were used as prototype databases for the three pure phases. The optical responses of the ''pure'' silicide phases were extracted from the measured SE spectra

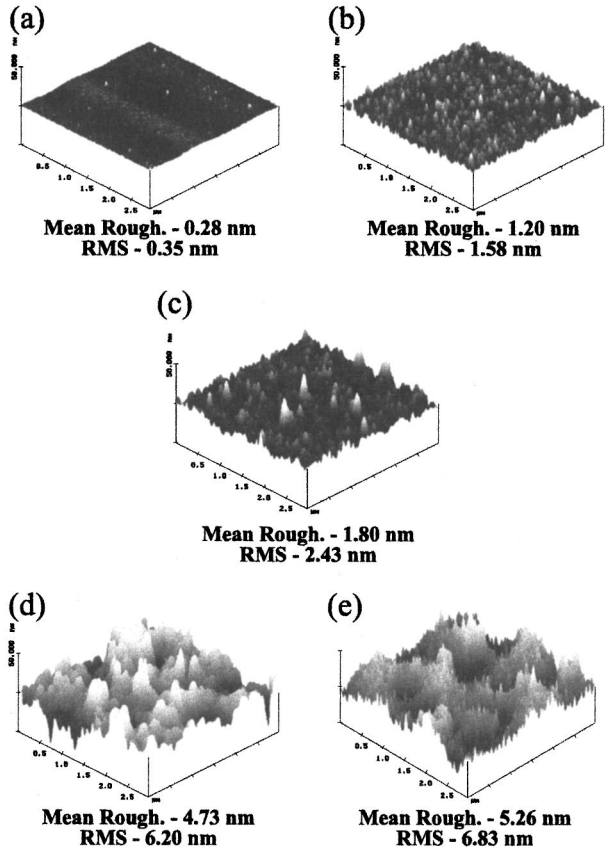

FIG. 2. AFM images, mean and rms roughness values for: (a) Ni on Si, and for samples annealed at (b) 250 °C, (c) 500 °C, (d) 800 °C, and (e) 1000 °C for 30 s.

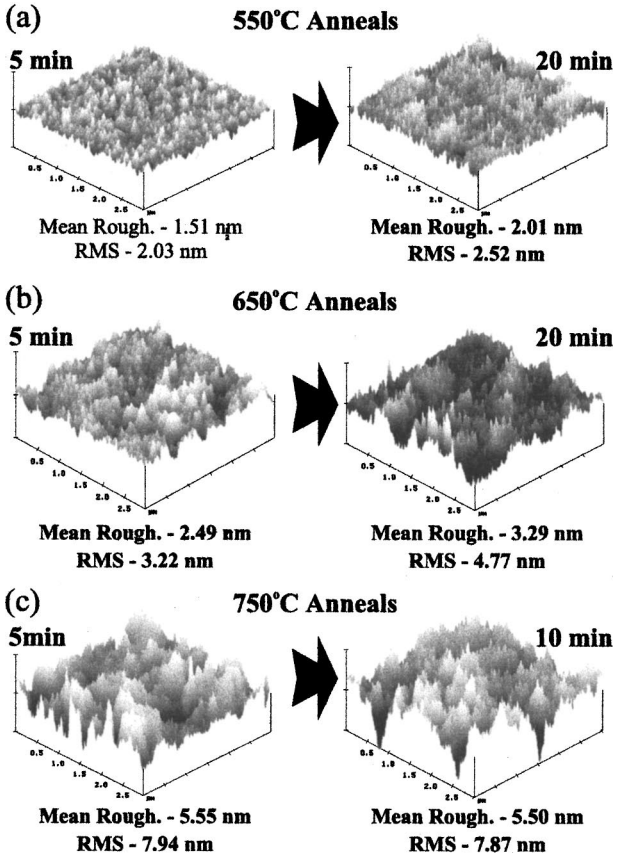

FIG. 3. AFM images, mean and rms roughness values for samples annealed at: (a) 550 °C, (b) 650 °C, and (c) 750 °C for longer times (5, 10, or 20 min as specified).

signal by fitting the data to an optical model [Fig. 5(a)] and varying the optical constants n and k of the silicides. Silicide and roughness layer thicknesses supplied to the models are the expected values based on a starting sample of 25 nm Ni on Si, and the measured roughness layer thicknesses from AFM analysis, respectively. The optical data were fitted to models with and without the roughness layer. The fits of the spectra for the 250 and 500 °C annealed samples, representing the Ni_2Si and NiSi phases, respectively, did not show significant changes with or without the inclusion of a rough-

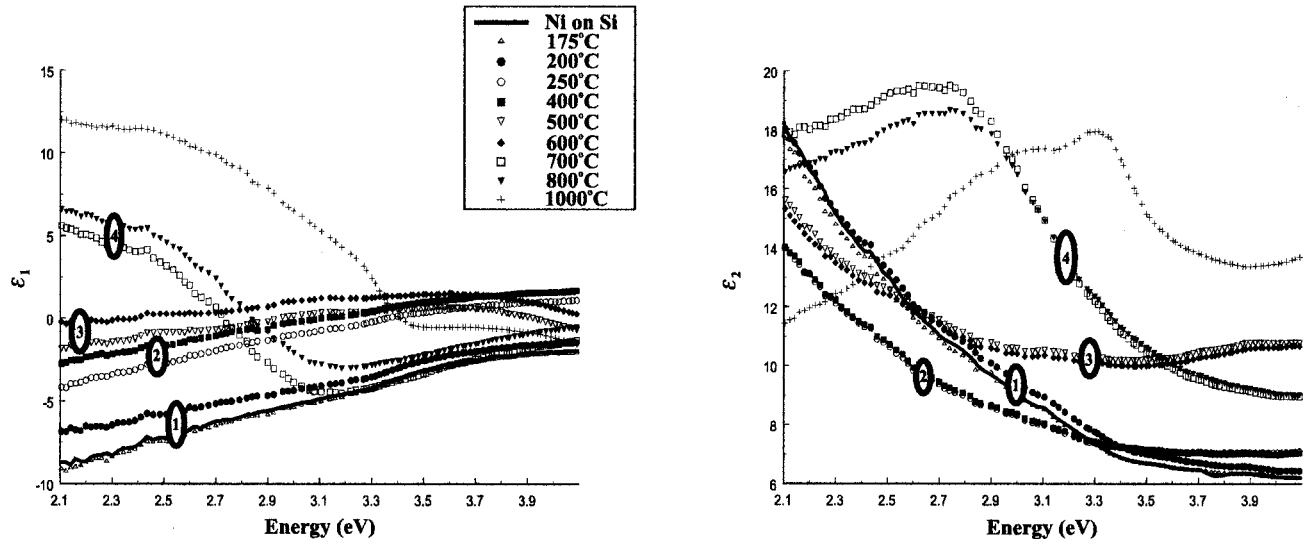

FIG. 4. SE spectra for samples annealed for 30 s. Also marked are four groups of spectra that represent predominantly: (1) Ni on Si, (2) Ni_2Si, (3) NiSi, and (4) $NiSi_2$.

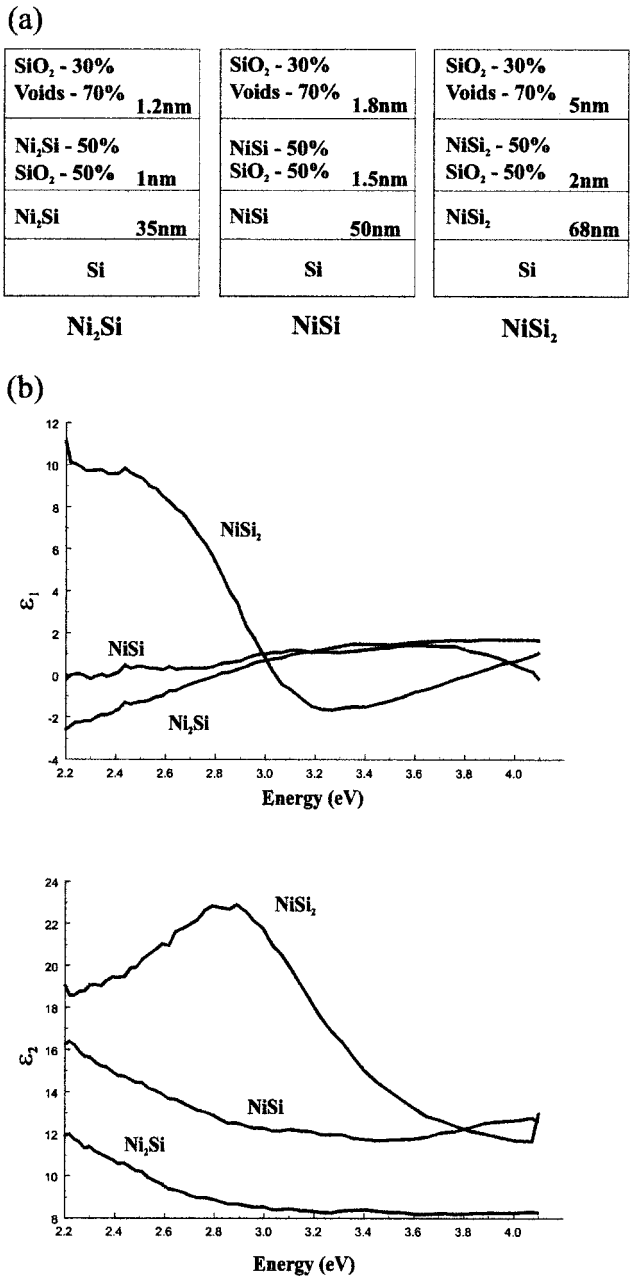

FIG. 5. (a) Ellipsometric models, and (b) SE spectra for the nickel silicides established as databases.

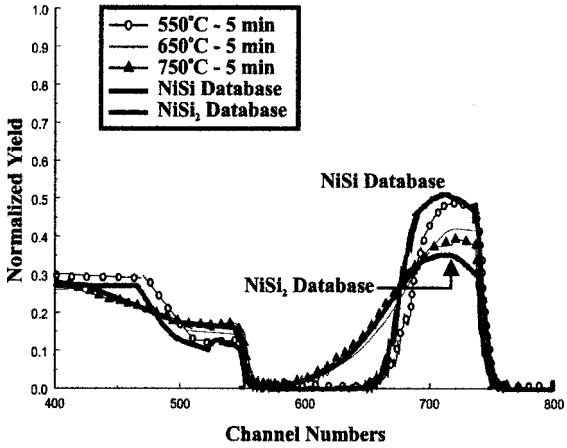

FIG. 6. RBS spectra for 5 min anneals at 550, 650, and 750 °C. Also shown are spectra for samples established as the NiSi and $NiSi_2$ databases (solid lines).

ness layer in the model. However, the 800 °C annealed sample, representing the $NiSi_2$ phase, showed about a 50% increase in ϵ_1 and ϵ_2 values when a roughness layer was included in the model. A large change in the optical spectra for the $NiSi_2$ phase, but not for the Ni_2Si and NiSi phases, corresponded to the smaller roughness layer thicknesses measured for the 250 (1.20 nm) and 500 °C (1.80 nm) annealed samples, and a thicker roughness layer for the 800 °C (5.26 nm) annealed samples. In order to obtain the optical properties of ''pure'' nickel silicide phases, a three layer model was used. Using this model the extracted optical properties are shown in Fig. 5. Experiments were also conducted to determine if these optical databases established using SE data collected at room temperature (RT) were also valid at higher temperatures. Results, discussed later, show that SE spectra collected at the higher temperatures were in fact nearly identical to the RT spectra, thereby indicating a very small temperature dependence of the optical properties in this temperature range, and validating the use of these databases for real-time data analysis.

RBS results for samples annealed for 5 min (Fig. 6), and SE for 5, 10, and 20 min (Fig. 7), show a transition from the NiSi to $NiSi_2$ phase with increasing temperature and time. For instance, both the RBS and SE spectra for the 550 °C anneal for 5 min, resemble the NiSi database. RBS spectra for the sample annealed at 750 °C for 5 min resembles the $NiSi_2$ database, and likewise the SE spectra appear similar to the $NiSi_2$ SE database. RBS and SE data were used to extract thicknesses and composition of various layers for these longer time annealed samples, and the proposed SE models are shown in Fig. 8(a). Roughness layer thicknesses in the models correspond well with the measured AFM mean roughness values (Fig. 3). As anticipated from the equilibrium phase diagram,[18] and as previous research[19–21] has shown, NiSi does not form until all the Ni has been converted to Ni_2Si. Similarly, $NiSi_2$ does not form until all the Ni_2Si has been converted to NiSi. It is also known that Ni, the mobile species, moves through NiSi during the transition from Ni_2Si to NiSi, as well as NiSi to $NiSi_2$.[19–21] Therefore, the SE data were modeled keeping in mind that only two nickel silicides can be present at any time, and that each silicide layer is a single phase.[19–21] The resulting SE models using expected silicide phases at the appropriate temperatures, yield good fits for SE spectra of the 550 and 750 °C anneals. Figures 8(b) and 8(c) show the measured and calculated SE spectra along with the RMSE values for the proposed models [Fig. 8(a)] for 550, 650, and the 750 °C anneal for 5 min. The 650 °C anneals give good relative RMSE values, but not visually similar spectra. The models show that NiSi is the predominant phase present at 550 and 650 °C. A relatively thin layer of $NiSi_2$ is also present between the NiSi and the roughness layer, and this layer increases in

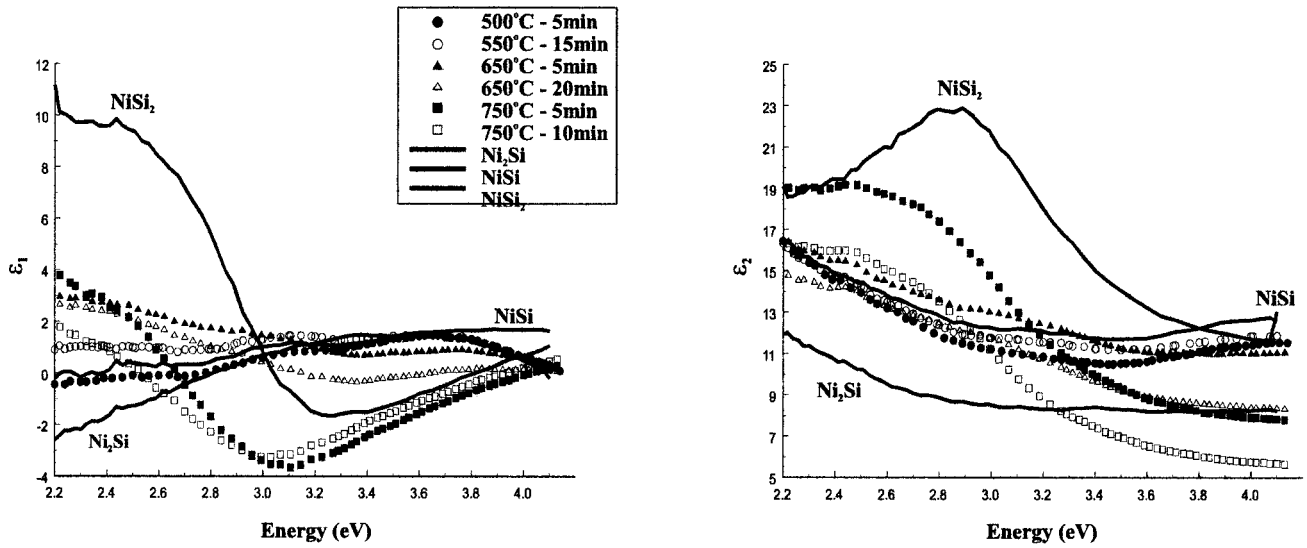

FIG. 7. SE spectra for samples annealed for longer times at 550, 650, and 750 °C. Also shown are the nickel silicide databases (solid lines).

thickness with increasing annealing temperature and time. RBS also indicates the presence of two phases, as is evidenced from the steplike features in the RBS spectra, which correspond to the NiSi and $NiSi_2$ database spectra (Fig. 6), between channel numbers 450 and 550. At 750 °C, all the NiSi has been converted to $NiSi_2$, and since some $NiSi_2$ begins to agglomerate, excess Si at the surface is present in the form of SiO_2, even below the roughness layer. The

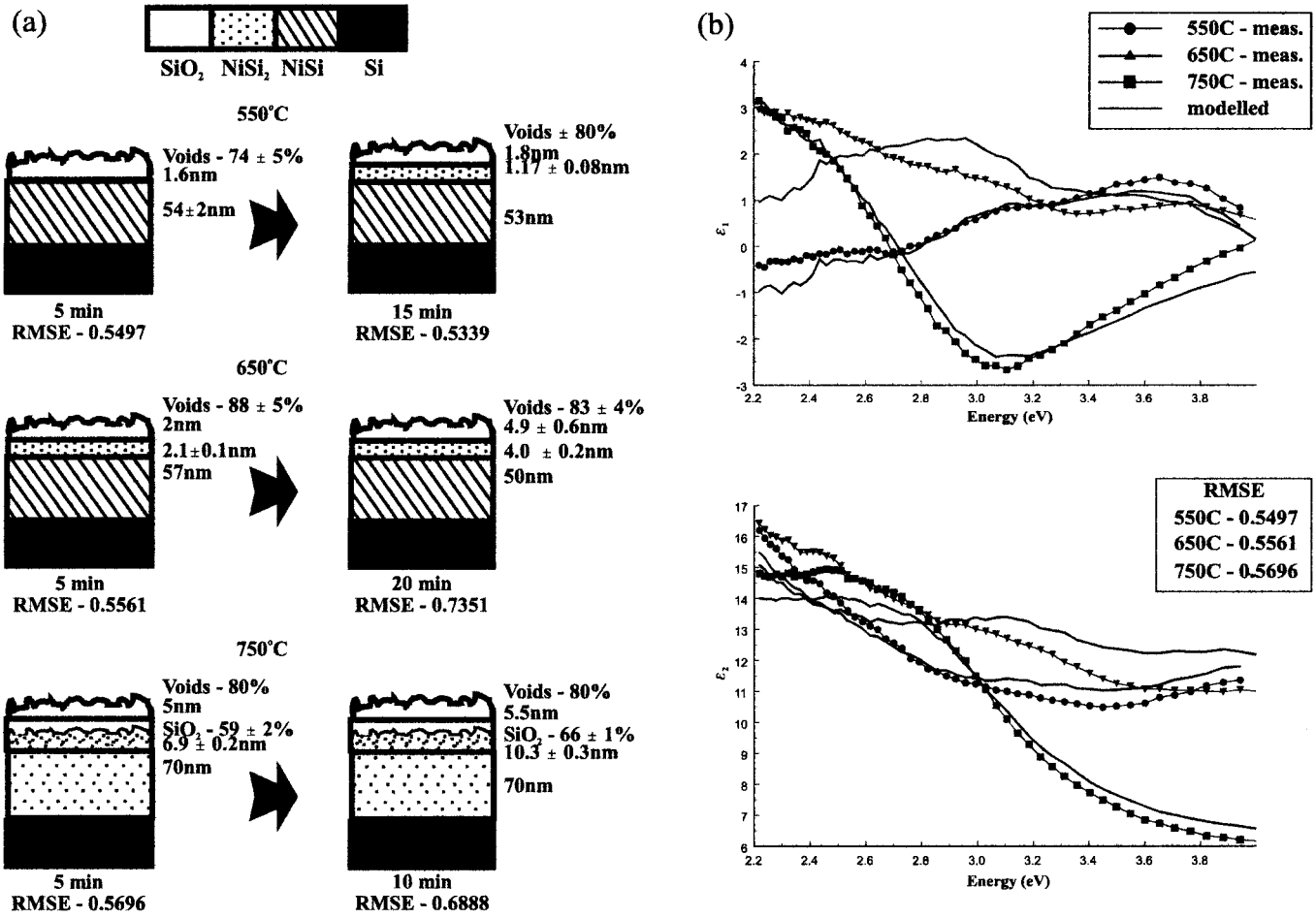

FIG. 8. (a) SE models for short and long time anneals, and (b) model fits for 5 min anneals at 550, 650, and 750 °C. Also shown are the RMSE values for the fits.

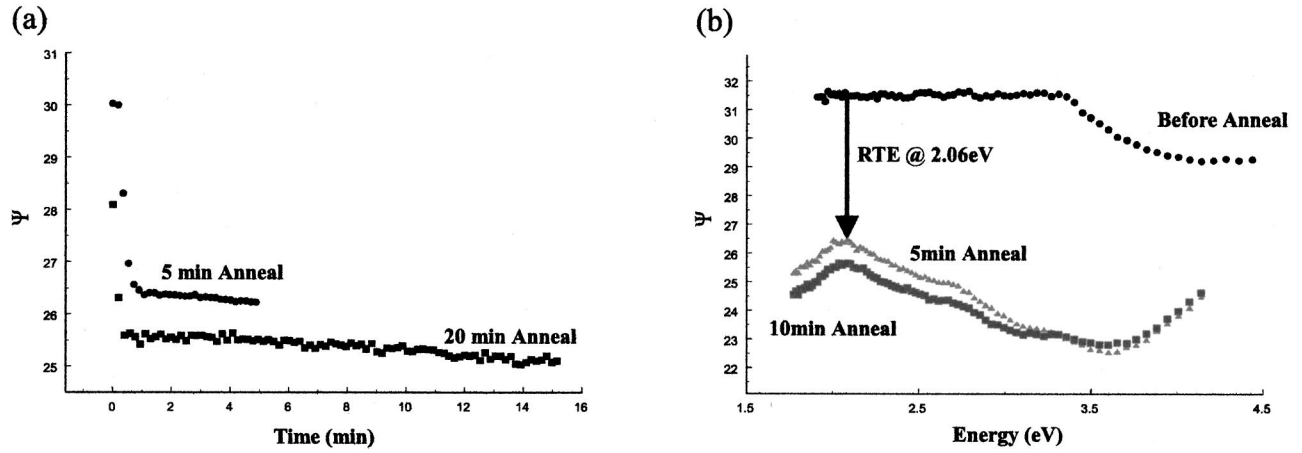

FIG. 9. (a) Single wavelength real-time, and (b) spectroscopic ellipsometry data for anneals at 550 °C for 5 and 20 min in the RTP system. RTE data taken at 2.1 eV.

thicknesses of NiSi and $NiSi_2$, as measured by RBS and SE, are also in agreement. For instance, the RBS spectrum for the sample annealed at 550 °C for 15 min, yields a 51 nm thick surface layer with a Ni:Si ratio of 46:54. According to the SE model, the sample has a 53 nm thick NiSi layer. Similarly, other samples also have comparable thickness values from SE and RBS models. As mentioned earlier, a slightly higher Si content observed by RBS was attributed to the presence of $NiSi_2$ and SiO_2 present on or near the surface.

AFM results for longer time anneals, as was discussed earlier, show a general trend of increasing roughness with increasing annealing temperature and time. This trend is also confirmed from the SE modeling, and the roughness values measured by AFM (Fig. 3) agree well with the roughness layer thicknesses obtained from the SE models (Fig. 8). Ellipsometry, as was demonstrated above, shows the presence of $NiSi_2$ at lower temperatures than is thought to be required for its formation, and both SE and RBS support the appearance of excess Si on the surface, present as SiO_2. While the SE and RBS findings are consistent with agglomeration, the similar surface morphology to the fully agglomerated sample is the strongest evidence for premature agglomeration. SE models show silicide layers covering the Si substrate, and thus suggest that the process of agglomeration is not complete. However, increasing roughness and thickness of the $NiSi_2$ layers, with increasing annealing temperature and time, is observed. In addition, AFM images reveal agglomerationlike surfaces with needlelike sharp features and deep valleys. The beginnings of agglomeration are clearly evident from SE models for the 750 °C anneal for 5 and 10 min, where all the NiSi has been converted to $NiSi_2$, and the layer above it is composed of $NiSi_2$ and SiO_2, which is characteristic of agglomeration where $NiSi_2$ agglomerates on the Si (present in the form of SiO_2) surface. AFM images for these two samples show increasing roughness and density of the sharp features with increasing annealing time. Based on the surface morphology observed, and the ellipsometric models, we conclude that agglomeration takes place, or at least begins, for longer time anneals at temperatures much lower than 1000 °C, the temperature where agglomeration is expected to occur. RTE was accomplished for long time anneals at constant temperature at an incident photon energy of 2.1 eV where a large change in ϵ_1 and ϵ_2 is observed in samples annealed at various temperatures (Figs. 4 and 7). Figure 9(a) shows the change in Ψ with increasing time as the sample is annealed for 5 and 20 min at 550 °C. A large initial change occurs as the temperature is rapidly raised to 550 °C, which levels after 1–2 min. However, a difference in Ψ is seen for samples annealed for the different times. Figure 9(b) shows the corresponding SE data. The SE models [Fig. 8(a)] show $NiSi_2$ forming at this temperature for the 20 min anneal, even though $NiSi_2$ should not form until 750 °C.[3] Another experiment was conducted where the temperature was raised from 25 to 500 °C in approximately 11.5 min. RTE data (Ψ versus time) at four different incident photon energies across the spectrum (2.2, 2.6, 3.0, and 3.8 eV) from this experiment are shown in Fig. 10(a). An abrupt change in Ψ is observed at approximately 1.8 min, corresponding to about 200 °C, where Ni_2Si is expected to form. SE data taken at different times during this temperature ramping stage are shown in Fig. 10(b). Spectra at 2.2 and 5.5 min match the SE data from which the optical database for Ni_2Si and NiSi phases, respectively, were extracted (shown in Fig. 4 for 30 s anneals at 250 and 500 °C, respectively). Ellipsometric models for the SE spectra at different times, given in Fig. 10(c), show the transition of phases as Ni is converted to Ni_2Si, and then converted to NiSi between 1.8 and 5.5 min. As the heating continues, the sample alignment changes due to hardware thermal expansion, which requires slight realignment of the ellipsometer. Once the temperature of 500 °C was reached, the ellipsometer was realigned and the SE data taken appear once again similar to the spectra taken after 5.5 min during the temperature ramping stage [shown in Fig. 10(b)]. The SE model is shown in Fig. 10(c) and can be compared to the SE model for the sample annealed at 550 °C for 5 min in the rapid thermal processing system (Fig. 7). In both systems, a thin layer of $NiSi_2$ begins to form after a 5

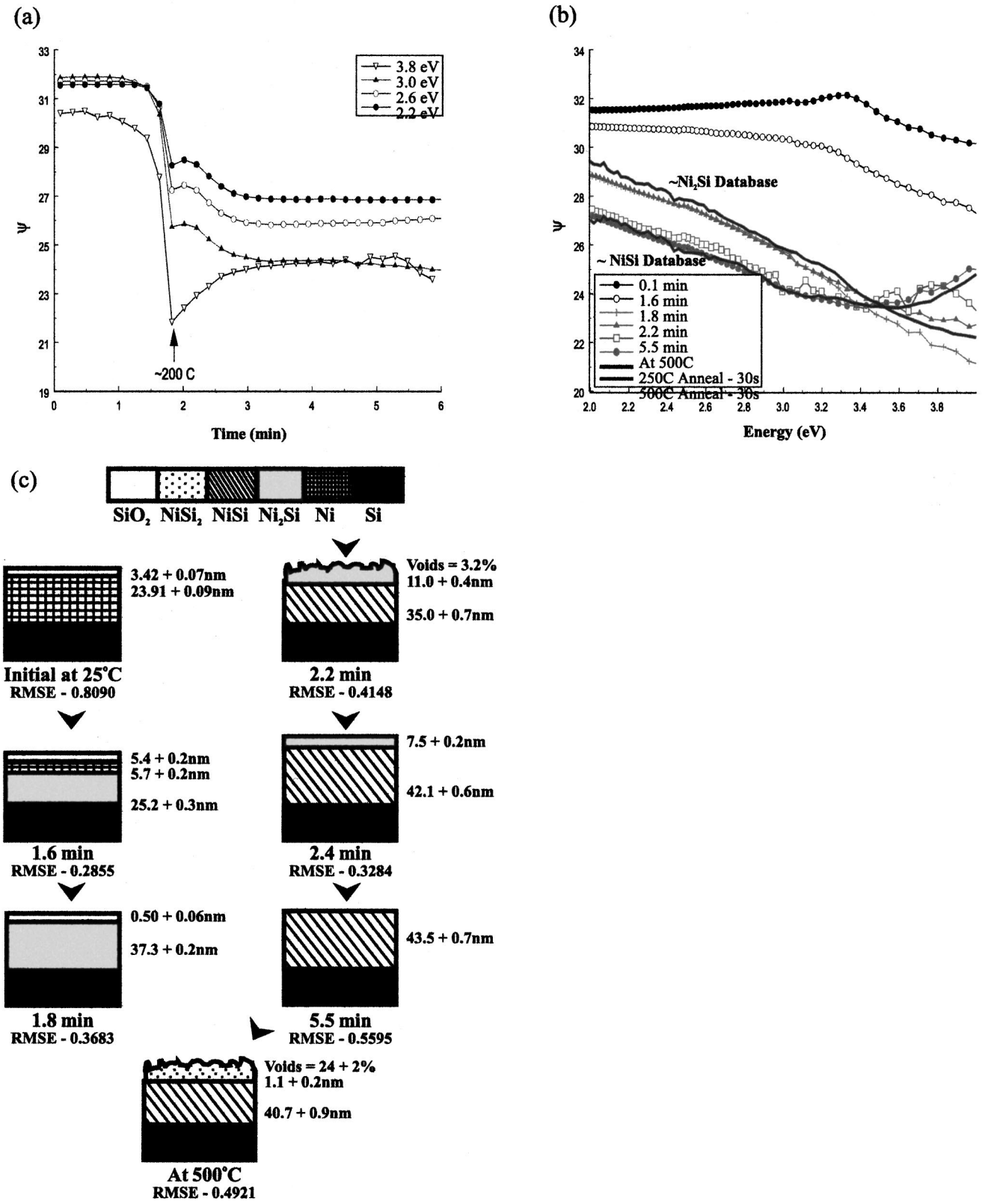

FIG. 10. (a) RTE, (b) SE, and (c) SE models for the temperature ramping stage during annealing from 25 to 500 °C over 11.5 min.

min anneal at 500 or 550 °C, where $NiSi_2$ is not expected to form.[3] The sample was annealed for 5 min after the temperature of 500 °C was reached, and the SE spectra taken did not show any change during this annealing process. After 5 min, the sample was cooled to RT. The spectra taken at RT are substantially the same as the spectra taken at 500 °C [shown in Fig. 10(b)], again demonstrating only a weak dependence of the optical properties on temperature in this range. This

assures reliability of the RT optical databases established in this study for real time monitoring of phase transformations at the formation temperatures.

IV. CONCLUSIONS

We have studied the phase transformations of nickel silicides using a variety of techniques and have established the temperature regime where the different phases form. We have measured optical property databases for Ni_2Si, NiSi, and $NiSi_2$. These optical databases for the three silicide phases can be used for ellipsometric modeling. In the process of studying the formation of NiSi, we have observed the onset of agglomeration for long time anneals at temperatures lower than the expected temperature of agglomeration. Real-time ellipsometry has been shown to be capable of following the phase transformations with increasing time and temperature. With the optical database now available, it is possible to monitor the phases present, measure thicknesses of various silicide layers (including the roughness layer), and identify the point where NiSi is the predominant phase.

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[1]Y. Hu and S. P. Tay, J. Vac. Sci. Technol. A **16**, 1820 (1998).
[2]D.-X. Xu, S. R. Das, C. J. Peters, and L. E. Erickson, Thin Solid Films **326**, 143 (1998).
[3]M. A. Nicolet and S. S. Lau, in *VLSI Electronics, Microstructure Science*, edited by N. G. Enspruch and G. B. Larrabee (Academic, New York, 1983).
[4]A. V. Amorsolo, Jr., P. D. Funkenbusch, and A. M. Kadin, J. Mater. Res. **11**, 412 (1996).
[5]T. Morimoto *et al.*, IEEE Trans. Electron Devices **42**, 915 (1995).
[6]E. G. Colgan, Thin Solid Films **279**, 193 (1996).
[7]F. Deng, R. A. Johnson, P. M. Asbeck, S. S. Lau, W. B. Dubbelday, T. Hsiao, and J. Woo, J. Appl. Phys. **81**, 8047 (1997).
[8]H.-W. Chen and J.-T. Lue, J. Appl. Phys. **59**, 2165 (1986).
[9]J. R. Jimenez, Z.-C. Wu, L. J. Schowalter, B. D. Hunt, R. W. Fathauer, P. J. Grunthaner, and T. L. Lin, J. Appl. Phys. **66**, 2738 (1989).
[10]K. N. Tu, E. I. Alessandrini, W. K. Chu, H. Krautle, and J. W. Mayer, Jpn. J. Appl. Phys. **2**, 669 (1974).
[11]Y. Gao, A. H. Mueller, E. A. Irene, O. Auciello, A. Krauss, and J. A. Schultz, J. Vac. Sci. Technol. A **17**, 1880 (1999).
[12]RUMP—Rutherford Backscattering Data Analysis Plotting and Simulation Package, Computer Graphics Service (Copyright 1987–1998).
[13]E. A. Irene, Thin Solid Films **233**, 96 (1993).
[14]E. A. Irene and J. A. Woollam, MRS Bull. **20**, 24 (1995).
[15]D. E. Aspnes, Thin Solid Films **89**, 249 (1982).
[16]R. D. Frampton, E. A. Irene, and F. M. d'Heurle, J. Appl. Phys. **62**, 2972 (1987).
[17]J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, in *Handbook of X-ray Photoelectron Spectroscopy*, edited by J. Chastain (Perkin Elmer Corp., Eden Prairie, MN, 1992).
[18]*Binary Alloy Phase Diagrams*, edited by T. Mallaski, J. L. Bennett, and L. H. Baker (American Society for Metals, Metals Park, OH, 1986), p. 1756.
[19]D. M. Scott and M. A. Nicolet, Nucl. Instrum. Methods **182/183**, 655 (1981).
[20]F. M. d'Heurle, D. D. Anfiteatro, V. R. Deline, and T. G. Finstad, Thin Solid Films **128**, 107 (1985).
[21]F. M. d'Heurle, C. S. Peterson, J. E. E. Baglin, S. J. La Placa, and C. Y. Wong, J. Appl. Phys. **55**, 4208 (1984).