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Formation of Nickel Silicide from Direct-Liquid-Injection Chemical-Vapor-Deposited Nickel Nitride Films

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Smooth, continuous, and highly conformal nickel nitride (NiN_x) films were deposited by direct liquid injection (DLI)–chemical vapor deposition (CVD) using a solution of bis(*N*,*N*′-di-*tert*-butylacetamidinato)nickel(II) in tetrahydronaphthalene as the nickel (Ni) source and ammonia (NH_3) as the coreactant gas. The DLI-CVD NiN_x films grown on HF-last (100) silicon and on highly doped polysilicon substrates served as the intermediate for subsequent conversion into nickel silicide (NiSi), which is a key material for source, drain, and gate contacts in microelectronic devices. Rapid thermal annealing in the forming gas of DLI-CVD NiN_x films formed continuous NiSi films at temperatures above 400°C. The resistivity of the NiSi films was 15 μΩ cm, close to the value for bulk crystals. The NiSi films have remarkably smooth and sharp interfaces with underlying Si substrates, thereby producing contacts for transistors with a higher drive current and a lower junction leakage. Resistivity and synchrotron X-ray diffraction in real-time during annealing of NiN_x films showed the formation of a NiSi film at about 440°C, which is morphologically stable up to about 650°C. These NiSi films could find applications in future nanoscale complementary metal oxide semiconductor devices or three-dimensional metal-oxide-semiconductor devices such as Fin-type field effect transistors for the 22 nm technology node and beyond.
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Metal silicides such as $TiSi_2$ and $CoSi_2$ have been commonly used as the contacts to the source, drain, and gate of complementary metal oxide semiconductor (CMOS) devices by the microelectronics industry.[1,2] As the dimensions of microelectronic circuits are being reduced, $TiSi_2$ has increased resistance at narrow linewidths (<250 nm) due to the low nucleation density of the low resistance C54-$TiSi_2$ phase,[3] whereas $CoSi_2$ was mainly limited by void formation in narrow polysilicon gates (<50 nm), which cause a drastic rise in resistance and by its very difficult formation on SiGe substrates.[4] To avoid the above problems, NiSi was investigated for the salicidation process because NiSi has many advantages including low resistivity (∼14 μΩ cm), low silicon consumption, low formation temperature, and no resistivity degradation in very narrow lines.[5] The silicon consumption in NiSi can be decreased by about 30% compared to $TiSi_2$ and $CoSi_2$. The low formation temperature of NiSi not only reduces the thermal budget but also limits dopant deactivation in shallow junctions. The NiSi films also have much smoother interfaces compared to films of $TiSi_2$ and $CoSi_2$ because the formation of NiSi is controlled by diffusion, whereas the formation of $TiSi_2$ and $CoSi_2$ is nucleation controlled. Such smooth interfaces could play an important role in the reduction of device leakage.[6]

NiSi has usually been made by annealing of sputtered or thermally evaporated Ni films on silicon.[7] As device sizes shrink, the step coverage of these physical-vapor-deposited Ni films inside narrow features is not expected to be adequate for use in future CMOS devices with closely spaced gate stacks or three-dimensional structures such as Fin-type field effect transistors.[8] Chemical vapor deposition (CVD) and atomic layer deposition (ALD) methods have been investigated to overcome this problem. Ni films prepared by metallorganic CVD methods, however, always incorporated a high content of impurities such as carbon.[9] CVD metal films deposited from some precursors also suffered from poor step coverage due to the limited volatility of the precursors.[10] Surface reactions of other precursors are too fast to allow a high step coverage.[11]

ALD of Ni films should provide high step coverage. Most ALD processes for Ni first deposited nickel oxide (NiO_x) and subsequently reduced the oxide to Ni by annealing the films with H_2 at a high temperature.[12] The introduction of oxygen during NiO_x deposition caused oxidation of the underlying silicon surface and thereafter agglomeration of the films during annealing (unpublished results). The ALD of Ni films by reduction of nickel bis(l-dimethylamino-2-methyl-2-butanolate), $Ni(dmamb)_2$, with molecular hydrogen (H_2) was investigated for the formation of NiSi.[13] A significant amount of carbon is distributed in the film, partly forming a Ni_3C phase. Such carbon contamination can degrade the film quality of NiSi by increasing sheet resistance and by forming NiSi with nonuniform thickness. Our group had previously deposited Ni films by ALD using the precursor bis(*N*,*N*′-diisopropylacetamidinate)nickel(II) and H_2.[14] These ALD films were, however, not practical for industrial applications because of the low thermal stability of the precursor and the low growth rate (∼0.04 Å/cycle) of the Ni films.

Direct liquid injection (DLI)–chemical vapor deposition (CVD) is a very attractive deposition method because DLI has the advantage of accurate delivery of high partial pressure of the precursor vapor. By using suitable solvents, solutions of solid precursors can be vaporized by DLI.[15] The high concentration of the precursor vapor during deposition is a key factor for achieving conformal step coverage and high growth rates. In this study, we employed a more stable metallorganic precursor, bis(*N*,*N*′-di-*tert*-butylacetamidinato)nickel(II) $[Ni(MeC(N^tBu)_2)_2]$ for DLI-CVD of NiN_x as an intermediate for the formation of NiSi. We deposited NiN_x films instead of pure Ni as the intermediate for NiSi formation because the incorporation of nitrogen into nickel has been shown to increase the thermal stability of NiSi and the electrical performance of transistors made using it.[16] The processes for DLI-CVD of NiN_x were described in detail elsewhere.[17] The step coverage of the NiN_x films inside deep holes with an aspect ratio of about 80:1 is nearly 100%. Rapid thermal annealing (RTA) of NiN_x films with thickness >20 nm at 450°C yielded continuous NiSi films. For thinner NiN_x films, initial steps of in situ annealing with H_2 at 160°C and capping with 10 nm thermally evaporated Ti were employed to prevent oxygen diffusion and film agglomeration so that continuous NiSi films having smooth and sharp interfaces with silicon could be achieved even for Ni thickness less than 6 nm.

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Experimental

The synthesis of $Ni(MeC(N^tBu)_2)_2$ is described in another paper.[17] A 40 wt % solution of $Ni(MeC(N^tBu)_2)_2$ in tetrahydronaphthalene (also called tetralin) flowed from a pressurized reservoir at room temperature through a Horiba-Stec liquid flow controller into an inexpensive thermal vaporizer.[18] The flow rate of the liquid solution was set to 0.1 cm^3 min^{-1}. The solution was vaporized in a tube heated to 150°C, where it mixed with a flow of 30 cm^3 min^{-1} of purified N_2. This mixture of Ni precursor vapor, solvent vapor, and N_2 carrier gas was then mixed with a flow of 60 cm^3 min^{-1} ammonia gas and another 30 cm^3 min^{-1} N_2 gas just before it entered the deposition zone. The total pressure in the deposition zone was regulated at 5 Torr by an MKS pressure controller. The partial pressures can be estimated from the ratios of flow rates to be about 0.12 Torr for the Ni precursor, 0.51 Torr for the tetralin, and 2.18 Torr each for NH_3 and N_2. The substrates rested a half-cylinder substrate holder inside a hot wall tube reactor (inner diameter: 36 mm) within a tube furnace. The substrate holder contained a small resistive heater and a thermocouple so that the substrates could be heated to a temperature slightly higher (typically 10°) than the walls. The purpose of this extra heating of the substrates was to cause any particles generated in the gas by the CVD process to drift away from the substrate by thermophoresis. Most depositions were carried out at a substrate temperature of 160°C.

Wafer-bonded silicon-on-insulator (SOI) (Soitec) and high resistivity (ρ = 160–240 Ω cm) (100) silicon wafer pieces were used as substrates. The substrates were treated with UV/ozone to remove organic contaminants and further dipped in 5% aqueous HF solution for about 10 s to achieve a hydrogen-terminated surface. Some of the as-deposited films were annealed in situ in the tube furnace in H_2 for 0.5–1 h at 160°C to yield pure Ni films without agglomeration.[17] A capping layer of 10 nm Ti was thermally evaporated onto some of the NiN_x films before annealing. The films were annealed to form NiSi at various temperatures from 450 to 550°C using a rapid thermal processor (RTP-600XP).

The sheet resistance of both the as-deposited and the annealed films was measured by a four-point probe station. The physical thickness of the films was measured by X-ray reflectometry (XRR). The amount of Ni deposited was measured by Rutherford backscattering spectroscopy (RBS). The nucleation and crystalline phases of both the as-deposited and the annealed films were evaluated by transmission electron microscopy (TEM), electron diffraction (ED), and X-ray diffraction (XRD). Planar Si TEM grids were prepared by wet etching of the back side of the Si substrates using a mixture of tetramethyl ammonium hydroxide and isopropyl alcohol solution as the etchant and thermal SiO_2 around 200 nm thick as the mask. The depth profile of the elemental composition was measured by an X-ray photoelectron spectroscope (ESCA SSX-100). For depth profiling, the sputter power is 4 keV; the raster size is 2–3 mm; the spot size is 800; and the resolution is 4. The surface roughness of the films was evaluated by atomic force microscopy (AFM). The thickness and morphology of the films was evaluated by scanning helium ion microscopy (SHIM). The phase formation during a temperature ramp at 180 K min^{-1} was studied using in situ XRD at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory.

Results and Discussion

A DLI-CVD NiN_x film was deposited with NH_3 at 160°C for 20 min. The NiN_x film thickness was determined by XRR to be 25 ± 1 nm. RBS determined the area density of Ni atoms to be 1.9×10^{17} cm^{-2}. The main phase in these films is Ni_3N, according to our previous XRD and ED measurements.[17] By combining the XRR thickness with the RBS number of Ni atoms and estimated N atoms, we deduce a film density of 8 g cm^{-3}, which is approximately the same as the reported bulk density of Ni_3N.[19] A NiN_x film on Si was annealed in forming gas at 550°C for 120 s, which increased the film thickness to 41 ± 3 nm. The sheet resistance decreased from 53.4 Ω/□ before annealing to 3.55 Ω/□ after annealing. The resistivity of the annealed film is 15 μΩ cm, a value close to the value reported for bulk NiSi.[20] Figure 1 shows the X-ray diffractogram (λ = 1.5406 Å) of the film after annealing. The XRD peaks confirmed the presence of NiSi.[21]

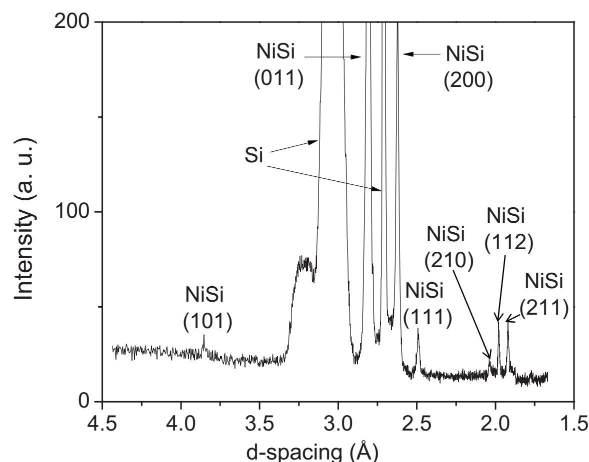

Figure 1. XRD spectra of a 25 nm thick NiN_x film after RTA.

All observed XRD peaks can be attributed to either a NiSi film or the Si substrate. For NiN_x films deposited on Si membranes, the samples were annealed at 400–550°C and thinned to electron transparency by ion milling from the back side of the silicon. Figure 2 shows the electron diffractogram of an annealed film, which confirms that NiSi was formed during annealing. Table I shows that the d-spacings from both the XRD and the ED agree well with the literature data for NiSi.[21] Figure 3 shows the depth-profile X-ray photoelectron spectroscopy (XPS) and the corresponding atomic concentration of the elements in the annealed film. After about 10 min of sputtering with the Ar plasma, which corresponds to the full removal of the surface layer, no C, N, or O was detected (sensitivity limit $<1\%$), showing that most, if not all, of nitrogen in the film is expelled during silicidation. The Ni/Si atomic ratio was 1 within the accuracy of the XPS analysis. These results confirmed that pure NiSi was formed by the RTA treatment of NiN_x films that are more than 20 nm thick.

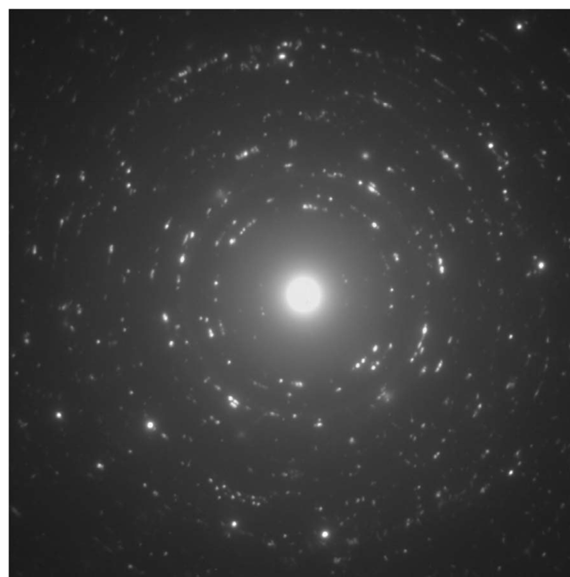

Figure 2. ED pattern of a NiN_x film after RTA treatment.

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Table I. XRD and ED interplanar spacings for a 25 nm thick DLI-CVD NiN_x film deposited on silicon given an RTA treatment at 550°C for 2 min. The planar indexes (*hkl*), calculated interplanar spacings (d), and intensities shown in this table represent literature data[21] for the NiSi crystal structure.

hkl	Calculated intensities	Calculated d (Å)	XRD d (Å)	ED d (Å)
101	153	3.842	3.85	
002	150	2.830	2.81	2.85
011	774	2.823	2.81	2.85
200	359	2.616	2.62	
102	130	2.489	2.49	2.50
111	218	2.485	2.49	2.50
210	112	2.040	2.04	
112	879	1.978	1.98	1.98
202	301	1.921	1.92	
211	1000	1.919	1.92	
103	334	1.775		1.78
013	155	1.632		1.63
020	284	1.629		1.63
270	85	1.383		1.37
114	129	1.260		1.25
222	127	1.242		1.25

When the thickness of a DLI-CVD NiN_x film was less than 20 nm, the sheet resistance of the film after RTA became too high to be measured by the four-point probe station ($>10^5$ $\Omega/\square$), which indicated that the film became discontinuous or agglomerated during annealing. The AFM images in Fig. 4a and b show that a 20 nm thick film became much rougher and agglomerated during annealing. The smooth surface of the underlying Si was also exposed in certain areas. Subsequent removal of the film by selective wet etching of Ni indicated that Ni did not react with Si. The oxidation of the underlying silicon surface may have prevented the reaction of Ni with Si and instead allowed Ni to diffuse over the oxide and agglomerate. The films were exposed to ambient oxygen and water vapor during transfer from the deposition system into the RTA system and also to oxygen and water impurities in the RTA atmosphere. Oxygen may have diffused through grain boundaries in the NiN_x film or directly through the film and then oxidized the silicon surface. This scenario is supported by the fact that no silicide was formed from a 25 nm thick NiN_x film that had been exposed in ambient air for months, whereas freshly formed NiN_x films of the same thickness formed continuous NiSi after annealing.

In situ annealing of some NiN_x films was done inside the deposition system in an atmosphere of flowing purified H_2 at 5 Torr and 160°C for 0.5–1 h. The XPS analysis showed that nitrogen was removed, leaving pure and dense Ni films that were better able to prevent oxygen diffusion. After this in situ annealing, these Ni films were transferred in air for subsequent RTA, and then any unreacted Ni was removed by wet etching. By this two-step annealing procedure, all NiN_x films with XRR thickness down to around 12 nm (the corresponding RBS "thickness" of Ni was around 9 nm) had dramatic reductions of sheet resistance, indicating that continuous NiSi was formed. The AFM image in Fig. 4c shows that the film with XRR thickness around 12 nm had a root-mean-square (rms) roughness of 2.4 nm after in situ annealing at 160°C. After RTA and the removal of the unreacted Ni, the rms roughness of the film was reduced to 1.8 nm, as shown in Fig. 4d. Figure 5a and b shows the top-view and cross-sectional scanning helium ion micrographs of the film after silicidation. The film is smooth and uniform, with a thickness increased to about 18 nm, confirming the formation of NiSi.

For films with thickness less than 10 nm, agglomeration becomes a more important degradation mechanism, which seriously limits the stability of NiSi films at a high temperature.[22] Adding metals such as Pt [4,23] and W [24] to the as-deposited Ni film or using Ti [25] and TiN [26] as capping layers are known to improve the stability of the resulting NiSi. Another possible degradation mechanism for our DLI-CVD NiN_x films is that the films become too thin to prevent oxygen from diffusing even after in situ annealing. The SHIM micrographs in Fig. 5c and d show that several cracks appeared in an about 7 nm thick NiN_x film (the RBS thickness of Ni is about 6.3 nm), which can provide pathways for oxygen diffusion.

To protect these thin in situ annealed NiN_x films from oxygen and agglomeration, we employed 10 nm thermally evaporated Ti as a capping layer before RTA treatment. The depth-profile XPS (Fig. 6) showed that after about 50 min sputtering, the Ti peaks disappeared and the Ni and Si peaks became dominant, which indicated that Ti did not significantly diffuse into the bulk of the NiSi film or bulk Si substrate during annealing. There might be an intermediate mixed layer of Ti and NiSi, but possible formation of TiSi at the top of the film should not affect NiSi underneath significantly. Some Ti may still reach interfaces through grain boundaries within the silicide film. Figure 7a shows a cross-sectional TEM image of an around 8 nm thick in situ annealed NiN_x film that was deposited on a single-crystalline SOI substrate and capped with 10 nm Ti before RTA. About 14 to 18 nm thick continuous NiSi was formed and the Ti layer stayed on top of the formed NiSi without obvious intermixing. The ED pattern in Fig. 2 from a planar TEM sample that was prepared under the same conditions confirmed the formation of NiSi. NiSi was formed similarly on highly doped p+ and n+ polysilicon substrates, as shown in the cross-sectional TEM images in Fig. 7b and c. A challenge for the integration of NiSi is that an

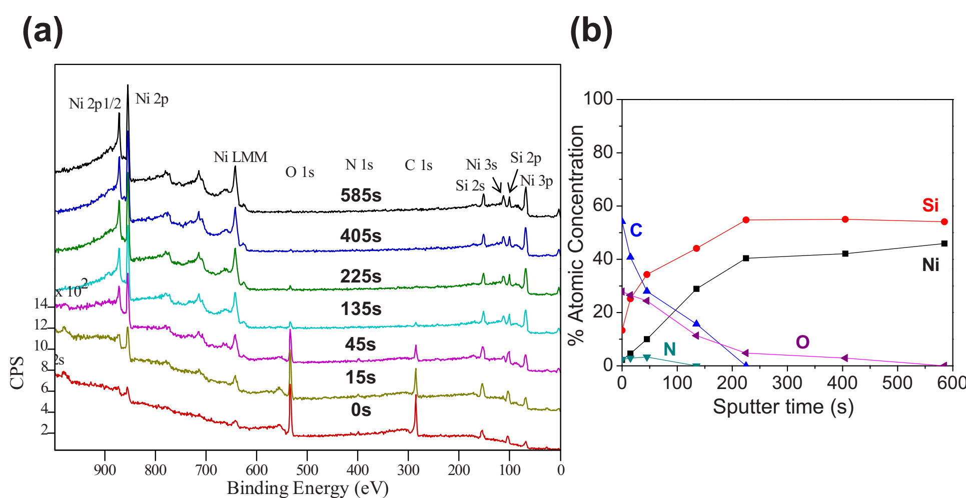

Figure 3. (Color online) (a) Depth-profile XPS spectra and (b) the corresponding elemental atomic concentration of a NiN_x film after annealing.

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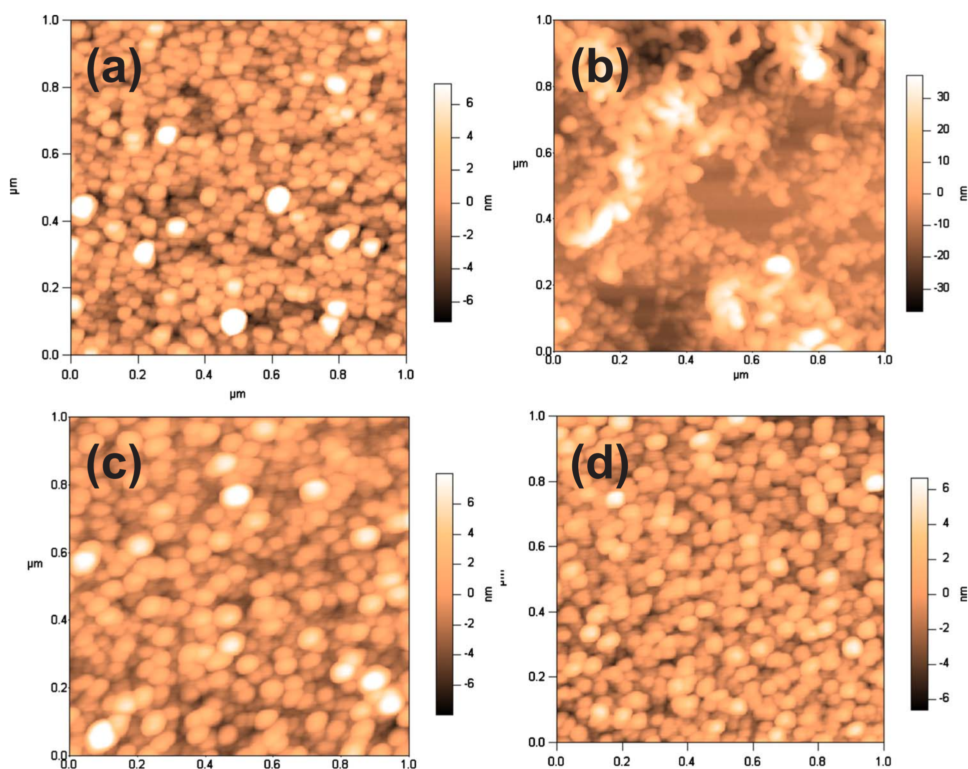

Figure 4. (Color online) AFM images of (a) an as-deposited 25 nm thick NiN_x film (rms roughness = 2.5 nm), (b) a 20 nm thick NiN_x film after ex situ RTA (rms roughness = 12.9 nm), (c) a 12 nm thick NiN_x film after in situ annealing (rms roughness = 2.4 nm), and (d) a 12 nm thick NiN_x film after in situ annealing and RTA and removal of unreacted Ni (rms roughness = 1.8 nm).

increased level of junction leakage current results partly from the presence of a rough interface between NiSi and Si.[6,27] From all cross-sectional TEM images in Fig. 7, we can see that the interfaces between the NiSi films and Si is quite smooth and sharp irrespective of crystal quality (Si or poly-Si) or dopant (n or p). These results indicated that Ti capping helps in preventing oxygen diffusion and film agglomeration for the formation of NiSi from DLI-CVD NiN_x films that have thicknesses less than 10 nm. NiSi formed from these

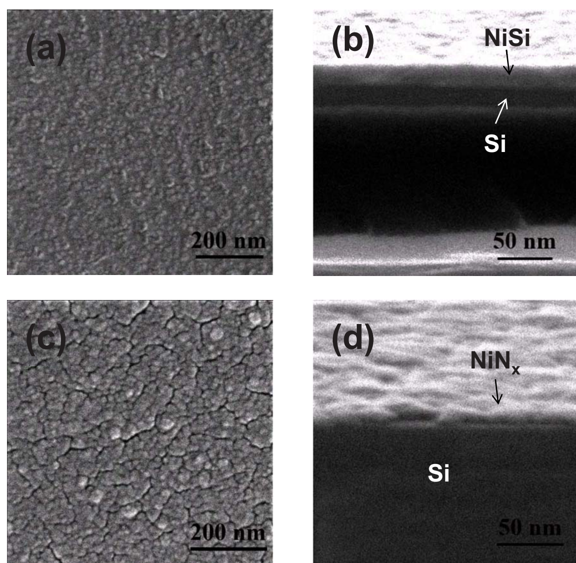

Figure 5. (Color online) [(a) and (c)] Top-view and corresponding [(b) and (d)] cross-sectional SHIM images of [(a) and (b)] ~12 nm thick NiN_x film after in situ annealing and RTA treatment and [(c) and (d)] about 7 nm thick NiN_x film after in situ annealing.

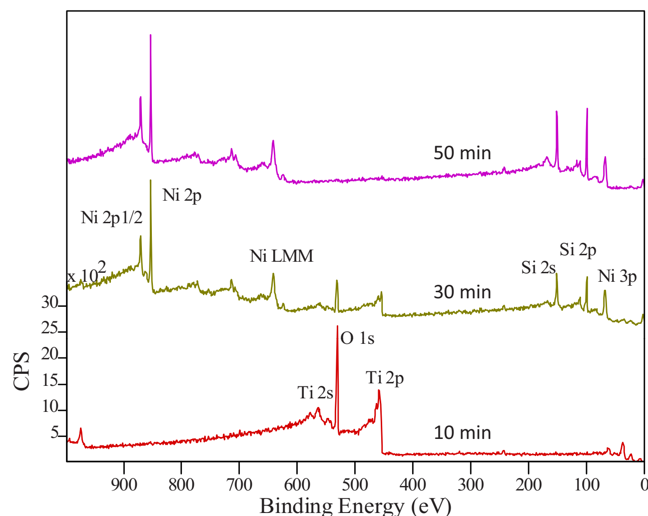

Figure 6. (Color online) Depth-profile XPS spectra of a 10 nm NiN_x film capped with 10 nm Ti after in situ annealing and RTA treatment.

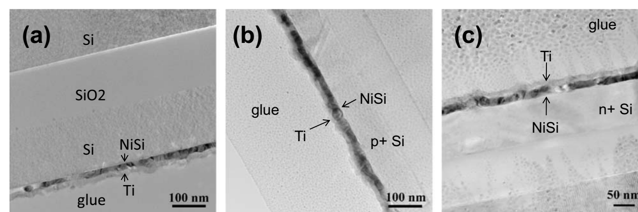

Figure 7. Cross-sectional TEM images of 10 nm NiN_x films deposited and annealed on (a) single crystalline SOI and (b) highly p-doped and (c) n-doped polysilicon substrates.

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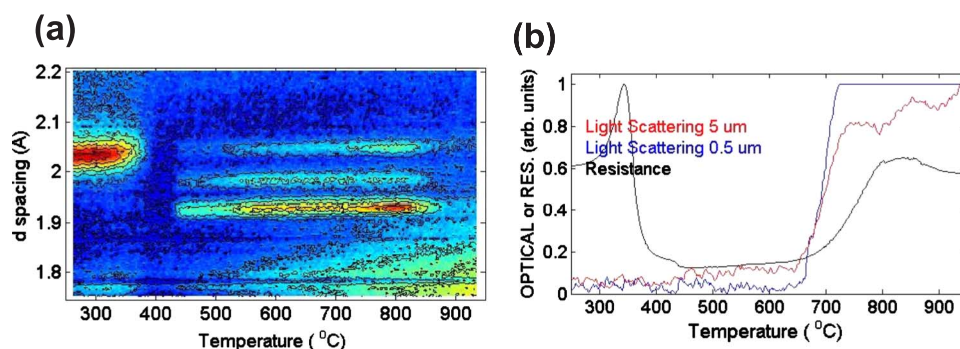

Figure 8. (Color online) The in situ XRD study of phase transformations as a function of processing temperature of an about 10 nm thick NiN_x film during annealing using the NSLS at Brookhaven National Laboratory.

thin NiN_x films has smooth and sharp interfaces with the underlying Si. Thus, NiSi contacts made from CVD NiN_x should produce transistors with a low junction leakage.[6,27]

Figure 8a shows the in situ synchrotron XRD (λ = 1.80 Å) pattern as a function of processing temperature. The XRD peaks of NiSi appeared at about 440°C and disappeared at about 850°C. The phase transformation during silicide formation was also simultaneously characterized by measuring the sheet resistance of the film as a function of processing temperature. As shown in Fig. 8b, the sheet resistance was minimized at about 440°C, which corresponds to the formation of NiSi. Above 650°C, there was an increase in sheet resistance, which suggests that the NiSi film started to agglomerate. The light scattering intensity acquired during the same anneal also showed a drastic increase in surface roughness above 650°C, confirming the agglomeration of the NiSi film.

Conclusions

The NiN_x films deposited from our DLI-CVD system had excellent step coverage and are suitable for application in future CMOS devices. Pure NiSi films with nearly bulk values of resistivity can be formed by RTA of NiN_x films that have a thickness of >20 nm. For thinner NiN_x films, in situ annealing and Ti capping were necessary to prevent oxygen diffusion and film agglomeration so that continuous NiSi films can be formed even from Ni films as thin as 6 nm. NiSi films formed from CVD NiN_x films have smooth and sharp interfaces with the underlying Si, indicating that a low junction leakage could be achieved with these NiSi contacts.

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