Initial stages of reaction and barrier heights in nickel silicide interface growth

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A time-resolved study of the initial stages of the formation of Ni-silicide growth using a pulsed-light annealing technique is described. The changes at the interface were measured as a function of the number of the annealing pulses. We used Auger electron spectroscopy to measure elemental composition and shapes of Si *LVV* and Ni *LMM* lines. Electrical changes at the interface were observed by Schottky barrier-height measurements. Ni diffuses into the Si, creating an amorphous interface layer at the silicon surface. A silicide phase emerges in this region by an amorphous-to-crystalline phase transition.

Transition-metal and near-noble-metal films (Ni, Co, Pd, Pt) in contact with single-crystal silicon undergo alloying reactions at relatively low temperatures, resulting in the growth of metallic silicides at the interface. These have important applications in device technology. Most studies[1] have concentrated on their growth kinetics, stoichiometry, electronic properties, and stability. Relatively few have addressed the more basic question of the mechanism of their growth, especially in the very early stages of reactions. Nucleation and growth are essential mechanisms in silicide formation. The presence of an initial interfacial silicide layer between Si and a metal has been assumed to explain at least phenomenologically the structure of first silicide phase in some metal-Si systems.[2,3] The origin of this layer and its role in silicide growth is however yet to be established. The chemical nature of the interface has been probed to understand these interfacial layers. Thus, Auger electron spectroscopy (AES) in conjunction with ion milling[4,6] as well as *in situ* examination[7] of growing planar silicide phases by x-ray photoelectron spectroscopy (XPS) have been used to study the chemical nature of the growth stages. Another approach for examining metal-silicon interaction is to sequentially deposit monolayers of metal on a clean silicon surface in ultrahigh vacuum and to study the chemical state of reacting atoms by photoemission spectroscopy or similar techniques.[8–11]

There have not been any highly time-resolved measurements of metal-Si interaction at realistic interfaces. We report here on a study of silicide formation with a time resolution of the order of 0.1 ms. The annealing is done by intense white light from a pulsed arc plasma discharge. The pulse width of the light from the plasma is ~ 60 μs. The experimental parameters are such that the thermal diffusion length $(k\tau)^{1/2}$ (where k is the thermal diffusivity of Si and τ the pulse duration), is much longer than the metal-silicon interface dimensions. Thus even for the short duration of the light pulse the thermodynamics of the system approaches that of steady-state annealing conditions. We can thus study the dynamics of silicide growth with a time resolution of a few tens of microseconds.

Our samples consisted of thin Ni films of thickness 300 Å vacuum deposited by electron-beam evaporation onto precleaned *n*-type (100) Si wafers. The vacuum system was equipped with cryotraps and had a base pressure $<10^{-7}$ Torr. Silicide formation was induced by light pulses from a plasma arc discharge in a gaseous mixture of N_2 and Ar in the ratio 2:3 at a total pressure of 500 Torr. The energy and pulse duration of the incident light were ~ 40 J/cm^2 and ~ 60 μs, respectively. Other details of the plasma light source have been described earlier.[12] The Ni-Si specimens were sealed in a Teflon holder with a transparent window to exclude plasma ions and electrons from bombarding the Ni surface.

The samples were irradiated with a series of light pulses and the corresponding changes in the elemental concentration profiles across the Ni(film)/Si(crystal) interface were analyzed by AES after each series of pulses. For clarity only three stages of the annealing sequence for 2, 15, and 25 pulses corresponding to total light irradiation of 0.12, 0.9, and 1.5 msec, respectively, have been shown in Fig. 1. Reduction of Ni concentration at the surface is likely due to the presence of monolayers of O and C which were detected by AES. A shift of the Ni-Si crossover point into the interior of the Si(crystal) side is observed (Fig. 1, curves *a* and *b*). This indicates the formation of an intermixed Ni-Si layer, probably as a result of interdiffusion process. Marker experiments[13] have shown that Ni is the mobile species in such systems. This suggests that diffusion of Ni into Si gives rise to Ni-Si intermixing in the early stages of pulsed annealing. In order to ascertain the chemical nature of the interface region as a result of this diffusion process, the remaining unreacted Ni film was selectively etched away in a weak solution of $H_3PO_4+HNO_3+H_2O$ (1:1:10), which is known[14] to have no effect on silicide and Si. This etching was carried out over a long enough duration to ensure complete removal of the unaffected Ni film. Fast-scan Auger differential spectra of the thus-exposed surface showed strong Auger signals for both Ni and Si while O and C signals were not observed, suggesting that their concentration was below the detection limit. The presence of both Ni and Si implies that one is probing into the Ni diffused region of the Si crystal surface. Relative changes in the Auger Si *LVV* line at 92 eV and Ni *LMM*

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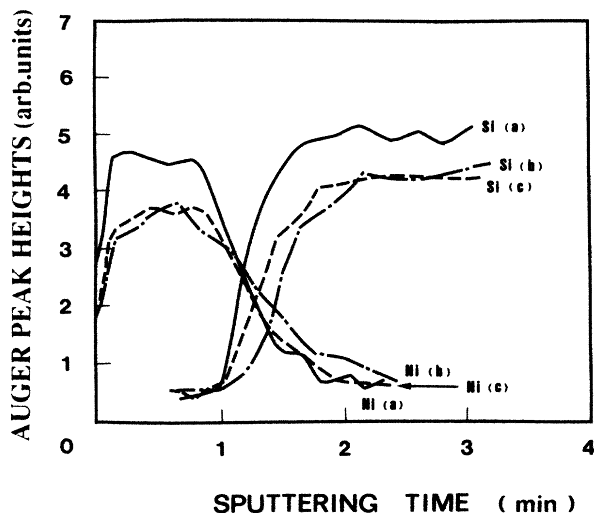

FIG. 1. Changes in Auger peak intensity as a function of sputtering time. The curves represent Ni and Si elemental composition after annealings by 2, 15, and 25 pulses, corresponding to total annealing time of 0.12, 0.9, and 1.5 ms, shown by (a), (b), and (c), respectively.

line at 848 eV on the thus-exposed interface were then measured after these were pulse-annealed for increasing periods of time. This is shown in Fig. 2. The observed Si *LVV* line shape, until about 0.9 ms of annealing, is typical of that of pure Si. On further annealing, changes in Si

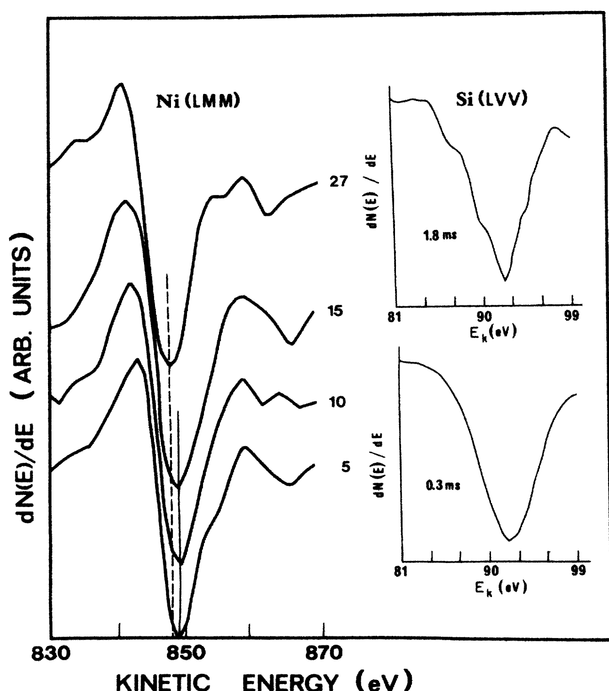

FIG. 2. The 849-eV Ni *LMM* Auger transition and shift. Numbers indicate the number of annealing pulses. The shift is ~ 1 eV. The inset shows a change in the Si *LVV* Auger line shape after total annealing times of 0.3 and 1.8 ms.

LVV line shape,[4,15,16] particularly the splitting at the higher-kinetic-energy side, indicate that Si is in an environment chemically different from free Si. Similarity of the shape of the Si *LVV* signal with those originating from a silicide phase[15,17] thus indicates the formation of silicide in the interface region. At the same time, we observe that the Ni *LMM* transition occurs at a kinetic energy ~ 1 eV less than that for free Ni. This is also typical of the Ni Auger signal in the silicide phase.[18] These observations indicate that the annealing over a duration of ~ 0.9 ms results in silicide growth within the intermixed Ni-Si region of the interface. It may be noted that what we are monitoring here are relative changes of the Auger signals at the interface as a function of the annealing time. The distinct changes in the shapes and positions of the Si (*LVV*) and Ni (*LMM*) Auger lines in the intermixed Ni-Si region therefore are not likely due to any possible microstructural effects at the interface caused by chemical processing.

Some recent studies have shown that a reaction between near-noble-transition metals, e.g., Ni/Si can occur at low temperatures[9,19,20] (~ 150 K). Interfacial silicides thus formed or present have been observed to extend to about a 10–15-Å-thick region at the interface.[21,22] Although these studies show the kinetics of the interfacial reactivity, and hence that formation of silicides is temperature dependent, further growth of silicides has not been observed to occur until the interface is heated to much higher temperature.[21,22] In our experiment no deliberate measures have been taken to suppress such interfacial reactions. It is possible therefore that about 10–15 Å of silicide may already have formed at the as-deposited interface. However, we did not detect such a silicide layer in the as-deposited samples, probably because the silicide, if present, was below the sensitivity limit of our Auger spectrometer in the presence of the background Si *LVV* signal.

The Auger line intensity ratio $I(\mathrm{Ni}(LMM))/I(\mathrm{Si}(LVV))$ suggests that the stoichiometry of the thus-formed silicide corresponds to NiSi. Photoemission spectroscopic studies have shown a graded composition of the interface,[9] with Ni at the silicide/Si interface being in a Si-rich environment and Si at the Ni/silicide interface in a Ni-rich environment. Others have observed interface composition[23] varying from NiSi to Ni and a mixed Ni_2Si and NiSi phase in case of thick Ni films.[17] In most cases of conventional furnace annealing, Ni_2Si is normally the first phase to grow. We have done glancing angle x-ray diffraction analysis of the exposed interface (Fig. 3). It is seen that a crystalline NiSi with (200) preferred lateral orientation grows at the interface.

The electrical nature of the changes at the interface in the early stages of the pulse annealing was examined by studying the behavior of a Schottky barrier diode (SBD). The barrier height is sensitive to the nature of the interfacial layer. All SBD's were fabricated on identically Ni-deposited specimens where a circular Ni area of 0.79 mm^2 was delineated by appropriate masking. The diodes were isolated by an oxide and no diffused guard rings were used. Both static parameters such as the Schottky barrier height ϕ_{BH} and built-in potential V_{bi}, and trans-

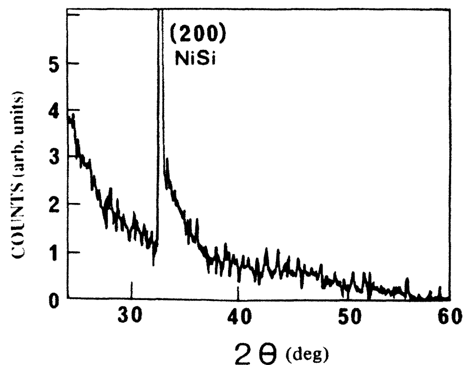

FIG. 3. X-ray diffractogram of the silicide phase at the interface.

port parameters such as the reverse saturation currents J_s and diode factor n were analyzed for any changes induced by the annealing sequence. The current transport follows the thermionic emission model and the forward current obeys the relation

$$I_F=[A_e A^* T^2 \exp(-\phi_{BH}/k_B T)]\exp\left[\frac{V}{nk_B T}\right],$$

where A_e is the effective diode area, A^* is the Richardson constant, and V is the impressed voltage. The term in square brackets represents the saturation current ($J_s A_e$). The barrier heights were determined by the activation energy analysis[24] of I_F at a fixed forward voltage, and also by the photoelectric method by studying the photocurrent dependence on the incident photon energy. Figure 4 shows the changes in ϕ_{BH} following annealing

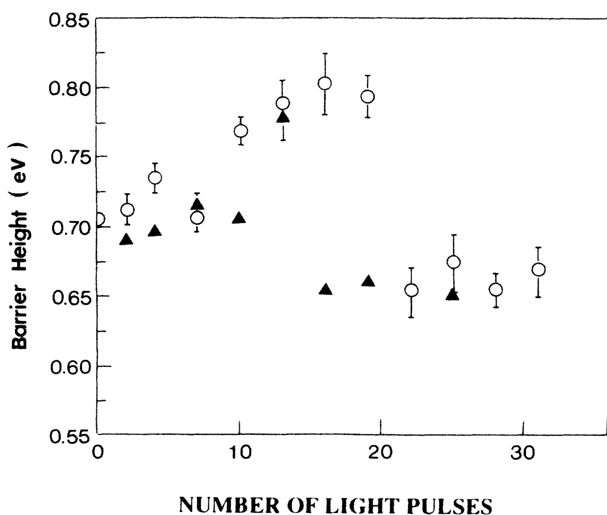

FIG. 4. Schottky barrier heights of the Ni(film)-Si(crystal) diode as a function of the number of annealing pulses, determined by activation-energy analysis (○) and by the photoelectric method (△).

with successive light pulses. The barrier height increases from an initial value of ~0.7 eV up to 0.8 eV after about 16 light pulses, corresponding to a total annealing period of about 0.96 ms. This increase essentially corresponds to the Ni-diffusion over this period as confirmed from the AES studies (Fig. 2) discussed earlier. The built-in potential V_{bi} was determined from the saturating values of the open-circuit voltage of a SBD with increasing white-light intensity. For all SBD's at different stages of pulsed annealing its values remained unchanged. But the diode factor n degraded from an initial value of 1.2 to 1.7. The saturation current J_s on the other hand decreased by a factor ~80, from 1×10^{-9} to 1.2×10^{-11} A/mm^2. On further light-pulse irradiation, the barrier height decreased sharply and finally reached a steady-state value. In this region ϕ_{BH} does not appear to vary in any systematic manner with further light pulses and remains clustered around 0.66 eV. The diode factor n for most of these diodes is around 1.15. The saturation current J_s however increased to ~6×10^{-9} A/mm^2. The barrier heights obtained by internal photoelectric method also show a similar behavior although their values were consistently lower.

It is known from spectroscopic studies[19,20] that about 10–15 Å of silicide can form spontaneously upon room-temperature deposition of Ni onto (100) Si. The Schottky barrier data described above show that in spite of the presence of a finite silicide growth at the interface, pulsed light annealing and the resultant formation of an intermixed Ni-Si layer can significantly affect the electrical behavior of the interface. The initial increase in diode factor n and decrease in J_s together show that current transport in these Schottky diodes is via some additional defect states. It is likely that these defects could form in the intermixed Ni-Si region as a result of Ni diffusion. It is clear from the above results that these defect states are sufficient to influence the Schottky barrier heights in a manner shown in Fig. 4. It has been pointed out by Schmid *et al.*[25] that an increase in the amount of silicide at the interface through an interfacial reaction can eliminate interface defects. Further, depending upon the extent of this silicide, an intrinsic interface may form which is no longer affected by extrinsic factors. Our observations of the changes in the diode factor n and reverse saturation current J_s are consistent with the formation of such an intrinsic silicide layer after ~0.9 ms annealing. This is evidenced by a decreasing value of n and increasing value of J_s. Also, the barrier height (Fig. 4) as well as n and J_s no longer vary with further annealing, which suggests that an intrinsic silicide/Si barrier has been formed. This is consistent with the Auger and x-ray data discussed earlier which show the formation of single-phase mononickel silicide at the interface. The observation of a sudden change in barrier height just prior to attainment of a steady-state value suggests that growth of NiSi is a result of an abrupt reaction. Further, since the Auger data of Fig. 2 were obtained after chemically exposing the interface by removing the balance of the free Ni film from the surface, the phase change to NiSi seems to involve essentially the Ni-diffused region. It appears therefore that the increase in the growth of NiSi occurs

by transformations in the Ni-diffused layer and that the NiSi layer now forms a homogeneous contact with the Si(crystal) surface to an extent that it now controls electrical properties of the interface. Before such a phase change occurs the barrier height continues to increase in the Ni-diffused regime with each successive pulse. This suggests that a threshold Ni diffusion into silicon is required before the rapid transformation leading to growth of NiSi. It also shows *a priori* that the Ni-diffusion and phase transformation processes occurring in that order are physically correlated. Accordingly we discuss the phenomena of initial increase in barrier heights attributed to Ni diffusion to help establish this correlation.

It is known that thermally stimulated diffusion of Ni into Si occurs by a dissociative process in which substitutional-to-interstitial interchange of Ni atoms in a Si lattice occurs through the formation of Si vacancies. A large fraction of diffusant Ni ($>2\times10^{15}$ atoms/cm^2) occupies tetrahedral[19] and octahedral[26] Si locations, thus introducing high strain energy into the Si lattice. Metal atoms, through coordination with Si, weaken the strong Si—Si covalent bonds,[27] forcing their breaking and reformation in order to achieve a chemical bonding configuration which satisfies the lowest energy requirements. The impurity states of Ni in Si are well known to be related to broken bonds at the impurity sites rather than to the *d* states on the Ni ion itself.[28] The diffusion of Ni increases the elastic energy[29] of Si and thus the kinetic process leads to development of an amorphous (disordered) Si phase at the interface. Existence of such layers has been shown by Raman scattering results on a Ni-Si system[30] and is consistent with an earlier model invoked to explain dependence of Schottky barrier heights of several silicides on their metal work functions.[31] Weakly reformed bonds and point defects in the amorphousized Ni-Si intermixed layer between the Ni(film) and Si(crystal) would give rise to localized states. The energy and density of these localized states in the band gap may vary depending upon the extent of disorder. The network defects in amorphousized layer are still identifiable with their crystalline counterparts. Hence there will be a peak in the density of states corresponding to the negatively charged state of a double Si vacancy at 0.4 eV below the conduction band.[32] The Fermi level may therefore shift rather than remain in its original position in the band gap. In the unannealed Ni-Si Schottky diode, the barrier forms when Fermi levels equilibrate. To accommodate surface positive charge due to uncompensated donors arising out of electron transfer to Ni, the bands are bent upwards. Upon annealing, as a result of the emergence of localized states induced by Ni diffusion, the net space charge is now determined by both the ionized donors and charged deep-defect acceptors. The Fermi level would thus shift towards the defect level giving rise to an increase in the barrier height.

One can estimate the changes in the magnitude of the barrier height by considering the balance of charges in the interface, those originating at the defects from the movement of the Fermi level with those in the space charge region of the Schottky diode. Such an analysis would be helpful in discussing the existence of the amorphous Ni-Si/*a*(Ni-Si) interface layer in the manner described above. One assumes[33] that the interface region containing defect charges is thin (~ 5 Å) and is located in a region $0<x<d$ and that all defects are localized in a plane at $x=d$ and that the crystalline Si is bound in the region $d<x<0$. Since we are interested in changes after the annealing we disregard here the effect of surface states which would invariably be present in an as-formed Ni/Si SBD. If these states were not capable of pinning the Fermi level, their effect is automatically reflected in a higher $\phi_{\rm BH}$ value for an as-formed SBD. The new Fermi-level position at the interface is obtained by equating the density of charged defects at the interface with those in the space charge regions. Accordingly,[33]

$$qN_{AS}^{-}=qN_a\left[1+gd\,\exp\left[\frac{E_A-E_F}{k_BT}\right]\right]^{-1}=\left[\frac{2\epsilon_S}{q^2}\int_{E_C(\infty)}^{E_C(d)}(N^{+}-N)dE_C\right]^{1/2}, \quad (1)$$

where E_A and E_F denote defect acceptor level and Fermi level, respectively, measured from the conduction band, ϵ_s is the dielectric constant (assumed same for amorphousized and single-crystal Si), N^+ is the ionized shallow donor concentration, and N is the electron concentration in the starting *n*-type Si(crystal). N_a is the density of defect acceptors and is proportional to the density of Ni atoms within the Si(crystal) surface layers and is given by[34]

$$N_a=ZN_n\int_h^\infty\left[\operatorname{erf}\left[\frac{h-x}{2\sqrt{Dnt}}\right]+\operatorname{erf}\left[\frac{h+x}{2\sqrt{Dnt}}\right]\right]dx\ , \quad (2)$$

where Z denotes the fraction of Ni atoms responsible for

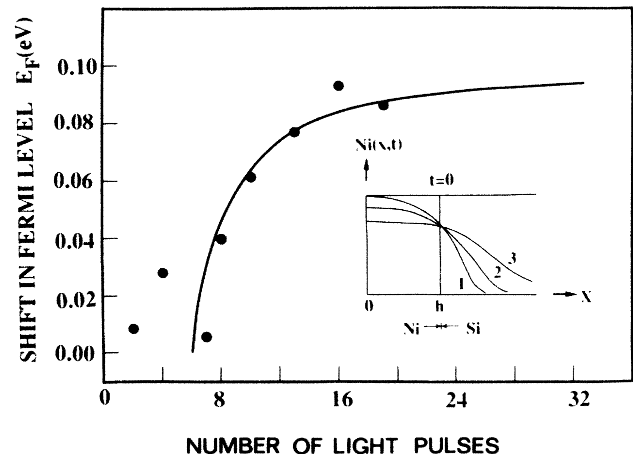

FIG. 5. The shift in the position of the Fermi level in the Ni(film)-Si(crystal) Si Schottky barrier diode as a function of the number of annealing pulses. The experimental points are obtained from Fig. 3 by subtracting the initial barrier height of the unannealed diode. The solid curve is obtained from theoretical analysis using Eqs. (1) and (2). The inset shows the Ni diffusion model used to evaluate density of Ni atoms in Si after pulse annealings (shown by 1, 2, and 3) and represents the situation experimentally identified in Fig. 1.

defects and N_n is the total number of Ni atoms in the Ni film. D is the diffusion coefficient[23] of Ni ($\sim 5\times10^{-8}$ cm^2/s) and n is the number of annealing pulses of duration t each. Changes in (E_C-E_F) at the interface in SBD Ni(film)/a(Ni-Si)/Si(crystal), $(E_C-E_F)_I$, with concentration of N_a and hence with N_n can be estimated using Eqs. (1) or (2). The barrier height of the as-formed Ni(film)/Si(crystal) SBD is related to E_C-E_F of the bulk Si(crystal), $(E_C-E_F)_B$, and is given by $\phi_{BH}=V_{bi}+(E_C-E_F)_B$, where V_{bi} is the built-in potential. We have observed that V_{bi} remains constant, so that the differences in Fermi levels of the unannealed and annealed SBD's $\Delta E_F=(E_C-E_F)_I-(E_C-E_F)_B$ would correspond to an increase in the observed barrier heights. This variation shown in Fig. 5 is in good agreement with the experimental data. Here the constant of proportionality Z is used as a normalizing parameter. It is worth noting that the Fermi level becomes almost stable after about 20 pulses, a point at which the silicide growth takes place by amorphous-to-crystalline transformation.

In conclusion, our studies distinguish an intermixed Ni-Si layer formation from the growth of an interfacial silicide. We also show that growth of silicide occurs within the intermixed layer, suggesting that manifestation of an intermixed region is the first stage of a silicide growth. In terms of a mechanism of silicide growth our findings show that first a disordered Ni-Si intermixed layer is formed at the interface, probably due to diffusion of Ni and Si. The silicide phase nucleates in this layer at some threshold value of Ni when this disordered (amorphousized) layer itself undergoes an atomic rearrangement. The driving force for this transformation is probably provided by the instability of the Ni matrix with its large number of Ni vacancies, as predicted by Tu.[27] The abrupt change in the barrier height suggests that silicide growth occurs in the amorphous Ni-Si region by an amorphous-to-crystalline transformation in less than 60 μs. Since only the amorphous region participates in this process, some diffused Ni still remains in the Si(crystal) side which may reinitiate the reaction through transport of more Ni across the NiSi layer in the usual manner.

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