

Changes in Optical Properties during Nickel Silicide Formation and Potential Impact on Process Results using Various Heating Methods

Woo Sik Yoo, Takashi Fukada and Igor J. Malik
WaferMasters, Inc., 246 East Gish Road, San Jose, CA 95112 U.S.A.

Nickel silicide was formed by heating sputtered Ni film on Si wafers in a stacked hotplate-based low temperature annealing system under 1 atm N₂. The annealing temperature was varied in the range of 200 ~ 450°C. Sheet resistance, spectral reflectance and spectral absorbance of Ni film on Si wafers were measured before and after annealing. Formation of desirable stoichiometric NiSi was observed by sheet resistance measurement, X-ray diffraction and cross-sectional transmission electron microscopy over the wide temperature range of 300 ~ 450°C. Phase change from Ni₂Si to NiSi was observed at approximately 300 ~ 350°C. The optical properties of nickel film, in particular spectral reflectance and absorbance, showed dramatic change during various stages of nickel silicide formation. Strong diffraction was observed from the patterned wafers. Microscopic reflectance and absorbance variation was observed from the patterned wafers as a result of the selective nature of silicidation. To minimize the negative impact of changes in optical properties during silicidation, radiation-based heating should be avoided as much as possible.

INTRODUCTION

Precise control of self-aligned-silicide (salicide) processes for contact formation is very critical to device performance. Among many silicide materials, nickel silicide is considered to be the most promising candidate to be used in advanced devices scaled down below one hundred nanometers due to its lower formation temperature, lower resistivity, smaller line-width sensitivity, and lower silicon consumption. [1, 2]

Despite the attractive nature of nickel silicide, formation of pure nickel silicide poses technical challenges due to the complex nature of this silicide. Nickel (Ni) film on a Si substrate goes through sequential phase transitions of Ni₂Si, NiSi and NiSi₂ from 200°C to 700°C. [2, 3] Each nickel silicide phase has different crystalline structure and electrical properties. A stoichiometric NiSi phase which gives the lowest resistivity among many nickel silicide phases is desired for advanced device applications. Development of a robust, high quality and repeatable

formation process yielding highly uniform NiSi is required.

There are many reports on NiSi formation using various types of annealing systems and annealing processes, including steps for sample preparation and annealing. [2-7] However, poor sheet resistance uniformity, poor repeatability due to nickel silicide phase mixing, agglomeration during annealing, NiSi/Si interface roughening and electrically active defect formation are typical issues. Sometimes a small amount of platinum (Pt) is added to the Ni which serves to suppress the undesired phenomena. The Pt, however, causes an increase in resistivity of the resulting silicide. and the benefit of low resistivity NiSi is compromised.

The authors believe that poor temperature control during nickel silicide formation in the temperature range of 200~450°C is partially responsible for the poor macroscopic and microscopic sheet resistance uniformity and repeatability. In the low temperature region, for NiSi process below 500°C, proximity heating in a hot wall based annealing system where

conduction and convection heat transfer are the primary heating mechanisms provides a uniform and repeatable process environment for heating Si wafers. Since the system provides a very uniform and repeatable thermal environment utilizing conduction and convection heating mechanisms, the on-wafer process results can be interpreted as material and structure (pattern) originated properties.

In this study, changes of electrical and optical properties of nickel silicide were studied using a stacked hotplate-based low temperature annealing system in the temperature range of 200~450°C under 1 atm N₂. Based on the changes of optical properties observed from Ni films on Si in the temperature range of 200~450°C, the potential impact on process results, using various heating methods, is discussed.

EXPERIMENTAL

Sputtered nickel (Ni) films (~10 nm thick) on (100) oriented p-type 200 mm blanket and patterned silicon (Si) wafers were prepared. Ni films were deposited on p-type Si by two different sputtering conditions (condition A and B). The Si wafers with Ni film were annealed in the temperature range of 200~450°C using a hotplate-based low temperature annealing system (WaferMasters' Stacked Annealing Oven (SAO-200LP)). All wafers were annealed in N₂ at 1 atmosphere for 5~10 min. in the following manner. The wafer is placed on three small standoffs between heated aluminum hotplate stacks without touching the hot plates (Fig. 1). The distance between the wafer and (top and bottom) hotplates is kept at 10mm during annealing. Since conduction and convection are the dominant heat transfer mechanisms in this temperature range (200°C~450°C), compared to radiation, wafers are annealed very gently to a saturation temperature provided by the top and bottom hotplates. A detailed configuration of the annealing system and its thermal characteristics are published elsewhere. [8-10]

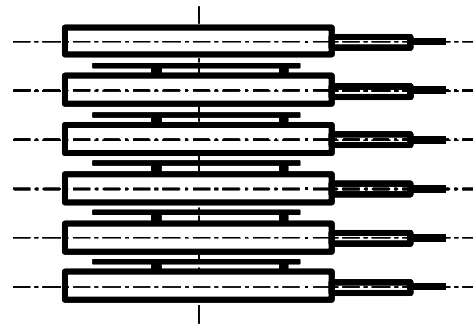


Fig. 1. Schematic illustration of wafers between stacked hotplates.

To understand the potential impact of macroscopic and microscopic temperature non-uniformity and non-repeatability, electrical and optical properties of Ni films on blanket and patterned wafers were measured as a function of annealing temperature. The crystallographic structure of the nickel silicide films was analyzed using X-ray diffraction and high resolution cross-sectional transmission electron microscopy (HRTEM).

RESULTS AND DISCUSSIONS

Blanket Wafers

Temperature Sensitivity

Change in sheet resistance after annealing of ~10 nm thick Ni films sputtered on p-type Si wafers was measured and plotted as a function of annealing temperature. Sheet resistance measurements were done at 49 points per wafer excluding 5 mm from the wafer edge. Figures 2 and 3 show the sensitivity of sheet resistance to annealing temperature for Ni films deposited under sputtering conditions A and B in 10 min annealing.

Sheet resistance and uniformity as deposited under sputtering condition A are ~20 ohm/sq. and ~2.0% in 1 σ before annealing. At 200°C, the sheet resistance increased from ~ 20 ohm/sq. (as-deposited nickel on Si) to ~ 45 ohm/sq. by forming the

high resistivity, Ni-rich silicide phase (Ni_2Si). As annealing temperature increases, the sheet resistance decreases to ~ 7.5 ohm/sq. at 450°C . Between 275°C and 300°C , the sheet resistance sharply decreased to ~ 11.0 ohm/sq. as the phase transition from the high resistivity Ni-rich Ni_2Si phase to a lower resistivity, stoichiometric NiSi phase takes place. The sheet resistance values continue to decrease to ~ 7.5 ohm/sq. by increasing annealing temperature up to 450°C .

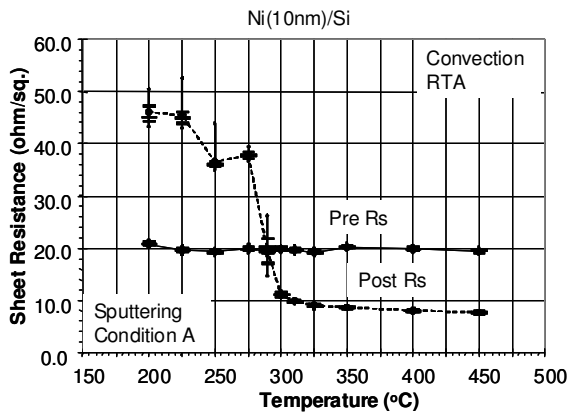


Fig. 2. Sheet resistance of Ni films on p-type Si before and after annealing at different temperatures. (Sputtering condition A)

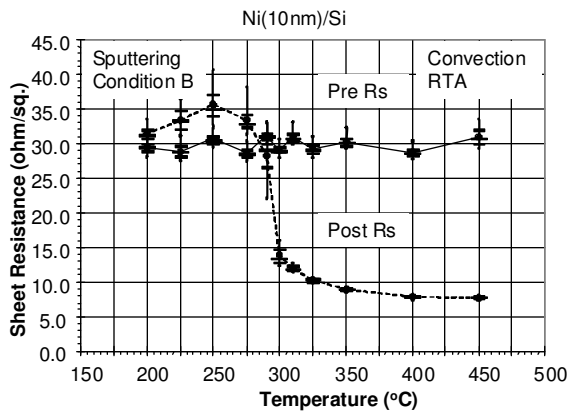


Fig. 3. Sheet resistance of Ni films on p-type Si before and after annealing at different temperatures. (Sputtering condition B)

For Ni films deposited under sputtering condition B, sheet resistance and uniformity before annealing are ~ 30 ohm/sq. and $2.5 \sim 4.0\%$ in 1σ . A large wafer-to-wafer sheet resistance variation of $>3.0\%$ (1σ) was present in the as sputtered Ni films. For annealing temperatures between 200°C and 250°C , the sheet resistance increased from ~ 30 ohm/sq. to ~ 35 ohm/sq. by forming the high resistivity Ni-rich phase silicide (Ni_2Si). Between 275°C and 300°C , the sheet resistance sharply decreased to ~ 14.0 ohm/sq. by phase transition from the high resistivity Ni-rich Ni_2Si phase to the lower resistivity stoichiometric NiSi phase. As annealing temperature increased, the sheet resistance value continued to decrease to ~ 7.5 ohm/sq. at 450°C .

There was no significant difference in phase transition behaviors between Ni films deposited under the different sputtering conditions A and B. The lower and consistent values of sheet resistance of the NiSi phase were obtained over a wide temperature range of $300^\circ\text{C} \sim 450^\circ\text{C}$. Changes in sheet resistance uniformity before and after annealing in the temperature range of $300^\circ\text{C} \sim 450^\circ\text{C}$, was usually less than 1% (1σ).

Reflectance

Spectral reflectance in the wavelength region of $220 \sim 830$ nm of as deposited Ni films under the sputtering conditions A and B is shown in Fig. 4. Significant difference of reflectance in the short wavelength region ($220 \sim 450$ nm) was observed. This is an indication of difference in film quality (grain size, Ni/Si interface roughness and possibly chemical composition) between sputtering conditions.

The change in spectral reflectance of nickel silicide films was monitored as a function of annealing temperature. (Fig. 5) The reflectance spectra changes as Ni films transform into the different nickel silicide phases. The Ni films annealed between $350 \sim 450^\circ\text{C}$, which resulted in sufficiently lower sheet resistance, showed very similar reflectance spectra even though the initial

reflectance spectra were significantly different depending on sputtering conditions (A or B). This confirms that lower resistivity nickel silicide (NiSi) is stable over this wide temperature range. Ni₂Si films, which formed at lower temperatures (200°C), showed different spectrum profiles from those of NiSi.

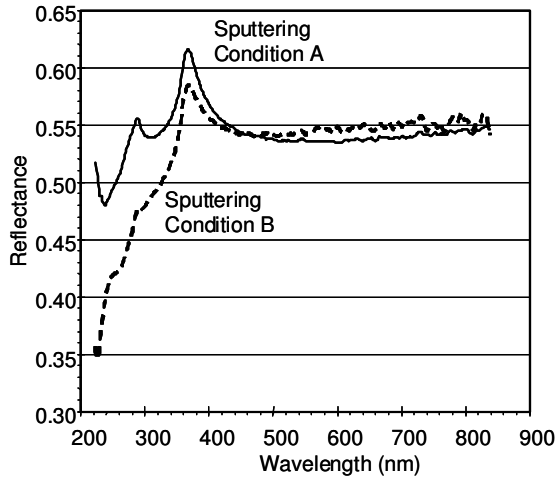


Fig. 4. Spectral reflectance of as deposited Ni films under different sputtering conditions.

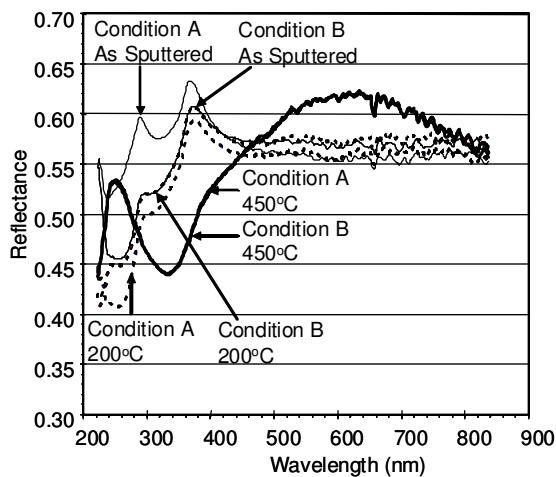


Fig. 5. Spectral reflectance change of Ni films under different annealing conditions. (Sputtering conditions A and B).

The significant variation in optical properties of blanket Ni films during nickel silicide formation (Ni to Ni₂Si and Ni₂Si to NiSi) at low temperatures suggests difficulties in wafer temperature measurement by optical pyrometry. It also suggests that the light absorption characteristics of Ni films keep changing throughout the entire silicidation process until completion. For lamp-based RTA, wafers (Ni films on Si) are heated by absorbing photon energy from the light source through optical interaction between the light source and the objects being heated. If the optical properties of the object being heated are constantly changing, the light absorption rate will change accordingly. This will create undesired temperature effects even under constant photon illumination.

In reality, blanket Ni film is deposited on a Si wafer and NiSi will be formed in a selected area. As one can imagine from the spectral reflectance curves in Figs. 4 and 5, optical properties of the masked areas and unmasked areas are different, as NiSi formation takes place. This will give rise to thermal non-uniformities, the magnitude of which will depend on the pattern size and density. Thermal non-uniformities will be generated even under an ideal, isothermal process environment. The microscopic temperature non-uniformity will be much more significant when radiation heating is employed compared to non-radiation based heating because of the local impact of emissivity and other physical property differences in adjacent materials.

X-ray Diffraction

In the as deposited Ni films, a strong diffraction peak from the Ni (111) plane was observed in addition to the background signal of Si (200) regardless of sputtering conditions. Since a Si (200) peak is forbidden by the extinction rule, the peak appeared to be very weak. At 250°C, diffraction peaks corresponding to Ni₂Si (133), NiSi (011), NiSi (112) and NiSi (013) planes were observed. Above 300°C, X-ray diffraction peaks related to the low

resistivity, stoichiometric NiSi were dominant.

Patterned Wafers

Optical properties of patterned wafers are much different from those of blanket wafers. Patterned wafers are generally very reflective and diffract light. Figure 6 shows a typical diffraction pattern from a device wafer under laser beam irradiation perpendicular to the wafer surface. The diffraction pattern under laser illumination is a signature of the wafer device patterns. Similarly, diffraction occurs under illumination from the white (broad) spectrum of photon energy from any lamp. It is difficult to distinguish diffraction patterns from the broad spectrum of photon radiation from a point source at close proximity. When patterned wafers are illuminated at an angle of incidence, the broad spectral properties of the incident light is easily observed. Microscopic reflectance and absorbance variation was observed from different areas of the patterned wafers as a result of the variations in the pattern-specific diffraction properties and selective nature of silicidation.

The behaviors are quite similar to diffraction gratings used in monochromators. The diffraction gratings have a large number of parallel grooves in one direction. The groove density varies from hundreds to thousands lines/mm depending on the wavelength of interest. The distance between grooves is in the range of few μm ~ few hundred nm. Microscopic temperature non-uniformity induced by pattern size and density is often ignored. Selectivity of chemical reactions on patterned wafers can also induce microscopic temperature non-uniformity. However, it is difficult to quantify this microscopic temperature non-uniformity. In addition to this difficulty, the problematic nature of macroscopic (within wafer and wafer-to-wafer) temperature measurement and control, with problems of absolute uncertainty, repeatability, fluctuations (instability) and non-uniformity

in thermal processing systems has distracted engineers and scientists from the fundamental physics of chemical reaction phenomena.

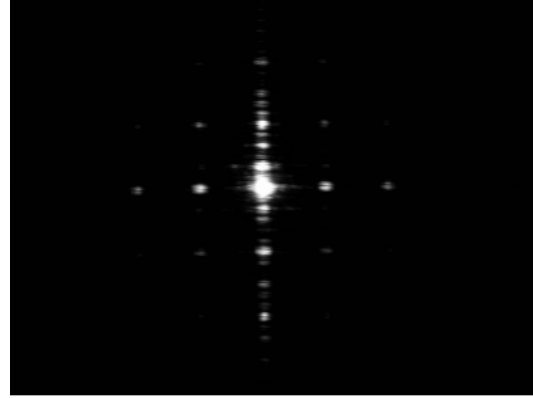


Fig. 6. A typical diffraction pattern from a device wafer under laser beam irradiation perpendicular to the wafer surface.

It is a general understanding that the process window becomes narrower as devices scale down. Precise temperature management on (patterned device) wafers becomes more important than ever. To gain good control of a process, all possible sources of uncertainty, variation and fluctuation including, device design, processing methodology (heating and reaction mechanisms) need to be reviewed and the best method selected, instead of resorting to temporary fixes.

Since the interaction between photons and Si wafers is involved in radiation-based heating, changes in the optical properties of Ni and Si, due to the intrinsic temperature dependence of the optical properties and selective chemical reactions formed on patterned wafers during any thermal process, can cause undesirable local, non-uniform process results on the scale of the minimum on-wafer feature size. The impact of this adverse effect is much more significant in patterned wafers, but it is difficult to quantify the effect using product wafers. Specially designed test element group (TEG) wafers are needed.

Detailed comparative studies on NiSi formation using radiation heating and convection heating systems have been reported recently. [6, 7, 11-15] The adverse effect of radiation heating and pattern-size dependent microscopic thickness non-uniformity of NiSi on TEG wafers were described with a proposed reaction mechanism for the microscopically non-uniform NiSi formation. A significant performance enhancement of devices due to the reduction of leakage current, has been reported by merely changing the NiSi formation method from radiation heating to convection heating. [14, 15]

Due to the intrinsic temperature dependence of optical properties of Si and selective chemical reactions on patterned Si wafers, wafer heating using light sources is likely to be problematic. To minimize the unwanted process variation and adverse pattern related effects (from density, size, structure and materials), which arise from the physics of the complex optical properties of the wafers, hot-wall based, non-radiation heating is desirable. Since the hot-wall based system controls the *process environment* and temperature instead of the difficult to monitor and control wafer temperature, very uniform and repeatable wafer processes are easily achieved. The process results are much less pattern sensitive compared to radiation based annealing process.

SUMMARY

The nickel silicide formation process was studied using a hotplate-based low temperature annealing system under 1 atm N₂ in the temperature range of 200 ~ 450°C. Sheet resistance and spectral reflectance measurements have confirmed a wide process window of 350 ~ 450°C for the desired low resistivity, stoichiometric NiSi layer. This was in good agreement with XRD data. Potential changes in optical properties during low temperature nickel silicide formation makes hot-wall based, non-radiation heating more desirable for

accurate reaction and process control. Excellent nickel silicide uniformity and repeatability was obtained using a hotplate-based low temperature annealing system.

Changes in the optical properties of nickel films, in particular spectral reflectance and absorbance, were characterized at various stages of the nickel silicide formation process. Strong diffraction as well as microscopic reflectance and absorbance variation was observed from the patterned wafers. Potential negative impact of radiation-based heating on process results was discussed. Non-radiation based heating is recommended to minimize the negative impact of changing optical properties during silicidation.

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