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Nickel mono-silicide formation using a photo-thermal process assisted by ultra-violet laser

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ABSTRACT

Photo-thermal processing assisted by laser irradiation is proposed as a novel method to control the phase of nickel silicide with reduction in the diffusion of nickel into the silicon substrate. The third harmonics of Nd^{3+}:$Y_3Al_5O_{12}$ laser (wavelength, 355 nm) is used for photo-thermal processing. Optical and thermal simulations are performed to obtain an optimum thickness (30 nm) of the nickel film for photo-thermal processing and to predict the temperature profile of the nickel-silicon interface during laser irradiation. It is confirmed that Ni_2Si, NiSi and $NiSi_2$ phase are effectively formed at the laser energy densities of 15, 20–40, and 50 mJ/cm^2, respectively. We demonstrate that the phases of nickel silicide determined by Raman spectroscopy and X-ray diffraction analyses are in good agreement with those predicted by the heat transfer simulation. In addition, undesirable diffusion of nickel into silicon substrate is considerably reduced by instantaneous photo-thermal processing using the nano-second laser (pulse duration, 6 ns).

1. Introduction

In modern silicon-based device and photovoltaic device fabrication, metal silicides have been widely used to reduce the contact resistance in the source/drain and gate electrodes. Among the various metal silicides, nickel silicide has great advantages such as low sheet resistance, low reaction temperature for silicide formation, and low silicon consumption during the silicidation process [1–4]. A number of studies have been devoted to the formation of nickel silicide [5–10]. These studies have indicated that the phase that has the lowest resistivity is nickel mono-silicide, and that nickel diffuses rapidly into silicon [11]. During the conventional annealing time used in silicidation process, the nickel can be diffused into silicon to a depth of approximately hundreds of nanometers. The undesirable diffusion of nickel can be a critical problem for device properties since such lateral diffusion of nickel underneath the spacer causes anomalously large junction leakage. Therefore, it is important to form nickel mono-silicide with reduction in the undesirable diffusion of nickel into silicon. However, the fabrication of nickel silicide by furnace and the rapid thermal annealing (RTA) process has significant limitations in terms of reducing the diffusion of nickel, because of the long annealing time. Photo-thermal processing assisted by irradiation with an ultra-violet (UV) laser is an attractive alternative to conventional fabrication processes, as it reduces the thermal annealing time, and thus, the diffusion of nickel into silicon. Moreover, it can effectively reduce the thermal budget because this process can deliver large amounts of energy into confined regions of the device [12]. Excited electronic states created by the laser transfer the energy to the phonons and heat is generated within a confined region [13]. In this paper, we propose a photo-thermal processing using the third harmonics of Nd^{3+}:$Y_3Al_5O_{12}$ (Nd^{3+}:YAG) laser as a new method for the formation of nickel silicide. Furthermore, the laser beam that was shaped to have a flat-top from a Gaussian beam was used to improve the temperature uniformity of the region irradiated by laser. The purpose of this study was to control the phases of nickel silicide with the minimization of undesirable diffusion of nickel into the p-type silicon, followed by photo-thermal processing with variable laser energy densities. The phases of nickel silicide were analyzed by Raman spectroscopy and grazing incidence X-ray diffraction (GIXRD) measurements with x-ray wavelength of 1.541 Å, and the results are compared with those predicted using the simulated temperature profiles. The profile of nickel diffusion into silicon is also discussed.

2. Experimental details

2.1. Nickel film deposition

In this study, we used an e-beam evaporator to deposit nickel films on p-type Si (100) wafers with a resistivity of 1–10 Ω cm and deposition

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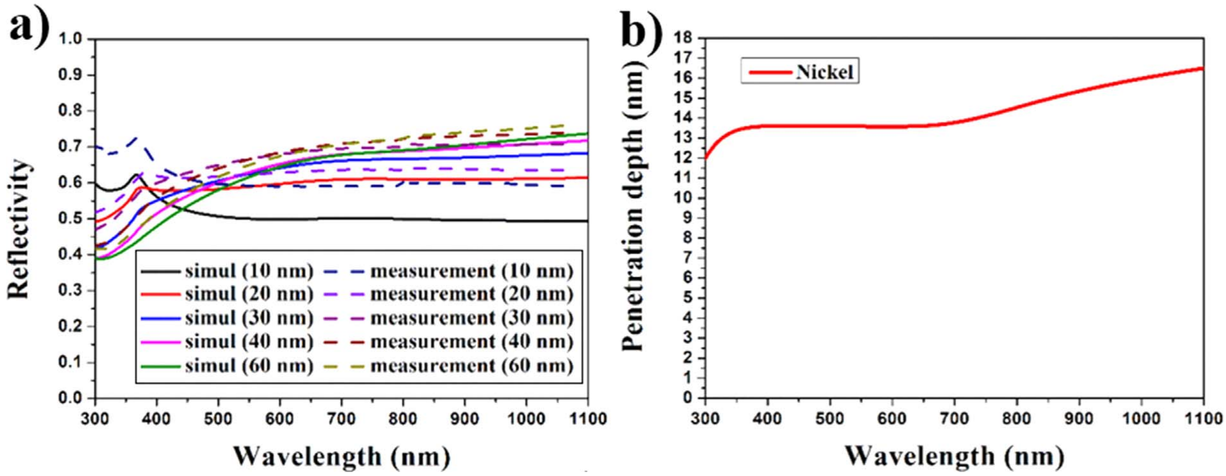

Fig. 1. (a) Simulated reflectivity (solid line) and measured reflectivity (dash line) of samples (thickness of nickel is 10, 20, 30, 40, and 60 nm) and (b) penetration depth as a function of wavelength.

rate of 1.0 Å/s. Before the deposition of the nickel film, the silicon substrate was cleaned with an RCA solution (NH_4OH:H_2O_2:H_2O = 1:1:5) at 85 °C for 20 min to remove organic surface contaminants. The silicon substrates were then treated in a buffered oxide etchant to remove the native oxides. Immediately, after etching away the native oxide, nickel films with thicknesses between 10 and 60 nm were deposited onto the silicon substrates. Prior to nickel deposition, a chamber pressure of 10^{-5} Torr was achieved in the evaporator chamber.

2.2. Optical and thermal simulation for photo-thermal processing

Before the photo-thermal process, optical simulation is performed to obtain optimum thickness of nickel during UV laser irradiation. The reflectivity of nickel with varying thickness was calculated using a well-known technique, the transfer matrix method. For the calculations, we used a commercial simulator (FDTD solutions, Lumerical Solutions, Inc.) with the provided function, "stackrt." Theoretical details regarding this are provided elsewhere [14].

The reflectivities (Fig. 1(a)) of the samples were measured using an ultraviolet-visible-near infrared spectrophotometer (Cary 5000, Agilent). In addition, the calculated reflectivity values of nickel films were compared with the measured values to improve the accuracy of the thermal simulation. From Fig. 1(a), the thickness of the nickel film used for photo-thermal processing was chosen as 30 nm, because the effect of the silicon substrate on the reflectivity of the nickel film is small at wavelengths ranging from 300 to 400 nm during UV laser irradiation. Owing to the transmission of light, the reflectivity of the sample is affected by the reflection of the silicon substrate at a film thickness below 30 nm. The penetration depth (Fig. 1(b)) was calculated from the relationship, 4πk/λ, where, k is the extinction coefficient of the metal at the wavelength, λ taken from the CRC Handbook of Chemistry and Physics [15]. Thereafter, analytical calculations by COMSOL Multiphysics were used to predict the temperature profiles of the samples during UV laser irradiation [16].

The simulation parameters used in the calculation are listed in Table 1. The temperature profile during photo-thermal processing can be described by the following volume equation of heat conduction:

$$c(T)\rho(T)\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}k(T)\frac{\partial T}{\partial x} + (1-R(T))I_0(t)\frac{e^{\frac{-x}{\delta_a}}}{\delta_a}, \tag{1}$$

where, c is the specific-heat capacity, ρ is the density of silicon, k is the thermal conductivity, T is the absolute temperature, t is the time, x is the depth from the surface, I_0 is the laser beam intensity, R is the reflectivity of silicon, and δ_a is the penetration depth.

Table 1
Simulation parameters for samples used in analytical calculation.

	Nickel (30 nm)	Silicon
C: Specific heat capacity [J/kg K]	455 (solid)	700 (solid)
ρ: Density [kg/m^3]	8890 (solid)	2329 (solid)
K: Thermal conductivity [W/m K)]	90.9 (solid)	130 (solid)
R: Reflectivity	0.543	0.5654
α: Absorption coefficient [1/cm]	7.44476 × 10^5	1.04 × 10^6

2.3. Photo-thermal processing assisted by UV laser

The laser annealing system used for photo-thermal processing is illustrated in Fig. 2(a). Laser-processing of a metal with laser-pulse durations that are greater than nano-seconds is considered a photo-thermal process [17]. Samples were irradiated using the third harmonic of a 355-nm-wavelength neodymium-doped yttrium aluminum garnet UV laser (Quantel, Q-smart) in a nitrogen-flushed chamber to limit the oxidation of the samples during the photo-thermal processing. The rate at which nitrogen was flushed into the chamber was 3 L/min. The 355-nm-wavelength UV laser was used with a flat-top beam shape and a pulse duration (full width at half maximum) of 6 ns. After homogenizing the UV laser beam, the energy distribution of flat-top beam profile was measured by beam profiler and the result is shown in Fig. 2(b). A homogenized UV laser beam with a rectangular flat-top beam profile (5 mm × 5 mm) was used to increase the uniformity of the temperature profile for the surface of the sample. According to the temperature profile obtained by simulations, the laser energy densities of the photo-thermal processing were ranged from 15 to 50 mJ/cm^2.

2.4. Measurements

Diffusion profiles corresponding to the diffusion of nickel into silicon were analyzed by time-of-flight secondary ion mass spectrometry (ToF-SIMS, ToF-SIMS 5, Ion TOF) in the dual-beam mode. For the detection of nickel, sputtering was accomplished using a Cs^+ sputter beam at an energy of 1 keV and current of 27.8 pA. The sputtering raster was 350 × 350 μm^2, while the analysis was made in positive polarity using a Bi_1^+ primary ion beam operating at 30 keV and a current of 1.03 pA, rastering over 100 × 100 μm^2. Both the beams bombarded the sample surface at an angle of incidence of 45°. The pressure in the main chamber was 2 × 10^{-8} bar. Before four-point probe measurements were performed to measure the sheet resistance [AIT, CMT-SR2000N], the unreacted nickel was removed by NH_4OH:H_2O_2:H_2O solution. The phase of nickel silicide was analyzed