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# Laser-induced direct formation of C54 $TiSi_2$ films with fine grains on *c*-Si substrates

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In this letter, we report on the direct synthesis of C54 $TiSi_2$ films with fine grains by pulsed-laser irradiation from Ti deposited on Si substrates, using a *Q*-switched Nd:YAG laser. The films were characterized using micro-Raman spectroscopy, high-resolution transmission electron microscopy, and atomic force microscopy. In comparison with the C54 $TiSi_2$ using the conventional rapid thermal annealing (RTA) of 35 nm thick Ti/Si, which has an average grain size of about 110 nm and film thickness of 50 nm, the laser-induced C54 $TiSi_2$ films vary from 13 to about 42 nm in thickness with different laser scanning speed and the grain size is 85 nm on average. The $TiSi_2$/substrate Si interface is smooth on the atomic scale. Our results demonstrate the unique advantages of the laser-induced formation technique and its potential in deep submicron semiconductor technology. We propose that the C54 phase is formed by solid-state diffusion, rather than melting. © *1999 American Institute of Physics.* [S0003-6951(99)03838-3]

As the density of microelectronic devices increases, low resistivity materials become more desirable for interconnects, especially in applications where the critical dimensions of transistors are less than 0.25 $\mu$m. Titanium disilicide ($TiSi_2$) is considered to be one of the most promising materials as contacts and interconnects for source, drain, and gate electrodes in complementary metal–oxide–semiconductor devices.[1] $TiSi_2$ has already been extensively applied in ultra large scale integration due to its many excellent characteristics such as low electric resistivity, high adhesion to Si substrate, and good thermal stability.[2] $TiSi_2$ can exist in two forms: the C49 phase and the C54 phase. The C49 $TiSi_2$ is a high resistivity (60–70 $\mu\Omega$ cm) metastable phase formed between 550 and 700 °C, while C54 $TiSi_2$ is a stable phase with low resistivity (15–20 $\mu\Omega$ cm) transformed from C49 $TiSi_2$ at 700–850 °C.[3] Currently, a two-step rapid thermal annealing (RTA) process is used for the silicidation of Ti on Si substrates. The C49 phase is first formed by low temperature annealing. After chemical etching of the unreacted Ti and a second annealing at higher temperature, transformation to C54 phase takes place. However, such transformation using RTA is extremely difficult in narrow lines[4] and thin layers[5] because C49 $TiSi_2$ grains are relatively too large to have sufficient triple points of grain boundaries which act as the nucleation sites for C54 $TiSi_2$.[6] To make $TiSi_2$ extendable for sub-0.25 $\mu$m technology, intensive efforts have been concentrated on increasing the density of nucleation sites, i.e., reducing the C49 $TiSi_2$ grain size, with moderate success. The various methods that have been attempted include preamorphization of Si by Xe,[7] and As,[8] and implantation through metal.[9] All the above methods succeeded in lowering the transformation temperature by 50–100 °C. In addition, thin silicide films of around 30 nm are also preferred in deep subquarter micron technology, where shallow junction (<100 nm) is applied. However, it is difficult to control the silicide layer thickness using conventional RTA. Reducing the Ti layer thickness is not an adequate approach, since it makes the transformation to C54 phase more difficult, as mentioned above.

Lasers have been utilized to induce silicide formation.[10–12] By pulsed-laser melting and intermixing of the metal and Si in liquid phase, a number of groups were able to obtain C49 $TiSi_2$, while no C54 phase has ever been synthesized with pulsed-laser irradiation. Very recently, Shamma *et al.*[13] have succeeded in the formation of C49 $TiSi_2$ on deep-submicron polysilicon gates, using pulsed excimer laser radiation. Followed by RTA at 850 °C for 20 s, C54 phase was formed even on 0.1 $\mu$m polycrystalline silicon (poly-Si) lines with very smooth film/substrate interfaces. In their experiments, a layer of amorphous silicon ($\alpha$-Si) was formed on the *c*-Si substrate by $^{75}As^+$ implantation, prior to the Ti deposition using the physical vapor deposition (PVD) technique. The presence of the $\alpha$-Si layer is the dominant factor responsible for the reduced interface roughness. They suggested that the $\alpha$-Si layer melted on laser irradiation while the *c*-Si substrate did not, due to the large difference in the melting point and thermal conductivity between them. Therefore, the formation of $TiSi_2$ is confined to the $\alpha$-Si layer. The authors also suggested that the grain size of the C49 phase was smaller than that achievable using RTA, but detailed results were not presented.

In this letter, laser annealing is applied to induce C54 $TiSi_2$ formation, which has many advantages over RTA. For example, with the laser annealing technique, energy is only

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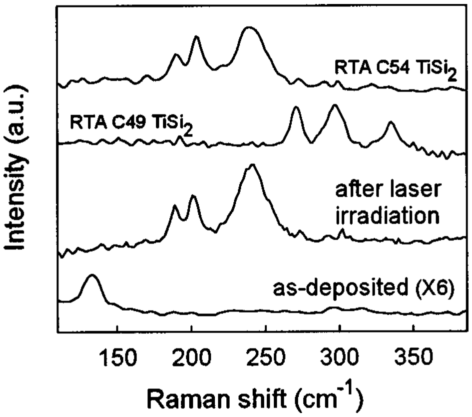

FIG. 1. Raman spectra of the as-deposited Ti film and laser irradiated sample. The weak peak at 137 $cm^{-1}$ represents the Ti phase. The three peaks at 193, 201, and 242 $cm^{-1}$ are due to the C54 $TiSi_2$. For comparison, Raman spectra of RTA C49 and C54 phases are also presented. Three peaks at 169, 297, and 333 $cm^{-1}$ are assigned to C49 $TiSi_2$. The Raman spectra verify the C54 phase formation on Ti/Si samples after laser irradiation.

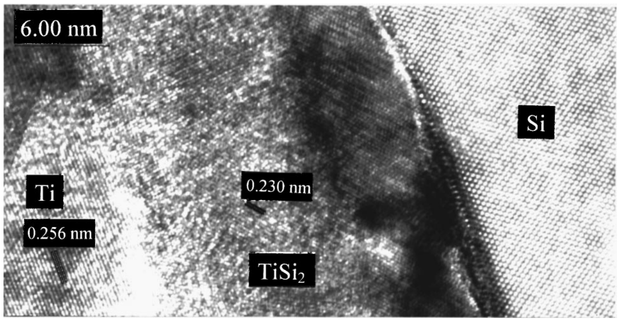

FIG. 2. High-resolution cross-sectional TEM image of a laser-annealed sample. The lattice in the middle represents that of a typical C54 phase and the lattice on the right is that of the Si substrate. Note that the silicide/Si interface is very sharp and smooth. The stoichiometry of the silicide layer is uniform and the thickness is measured to be 20 nm.

applied to the surface region,[11] enabling shallow silicide formation. Moreover, with its very fast ramping rate ($\sim 10^{10}$ K/s) and short laser pulse duration, this technique is expected to be able to generate fine grains.

In our experiments, the Ti/Si samples were fabricated by the standard PVD process, without preamorphization of the *c*-Si substrates. The (100) oriented *p*-type *c*-Si wafers were dipped into dilute HF to remove native oxide ($SiO_2$) immediately before being loaded into the rf sputtering system, which was then evacuated to a pressure below $5 \times 10^{-9}$ Torr. High purity Ar was subsequently introduced into the chamber to a pressure of 2 mTorr and Ti films of 35 nm in thickness were then sputter deposited on the Si substrate. To produce the C54 $TiSi_2$, the Ti/Si samples were irradiated by an NEC *Q*-switched Nd:YAG laser ($\lambda = 1.06\,\mu$m, $\tau_{FWHM} = 155$ ns) with a repetition rate of 10 kHz, the laser spot size of about 160 $\mu$m in diameter. The laser has a near Gaussian shape with an average laser power of 1.9 W, which corresponds to a density of 0.93 J/$cm^2$. A motorized stage was utilized to move the Ti/Si samples and the scanning speed varied from 0.1 to 1.0 mm/s. The experiments were carried out in the air ambient.

The laser-annealed samples were characterized using a number of techniques. A Renishaw System 2000 micro-Raman spectrometer, with a 20 mW He–Ne laser ($\lambda = 632.8$ nm) as the excitation source, was employed to identify the phases formed by the laser irradiation. Atomic force microscopy (AFM) was utilized to investigate the grain size, and a Philips CM300 high-resolution transmission electron microscope (HRTEM) operated at 300 keV was applied to study the structure and thickness of the film, as well as the film/substrate interface.

Figure 1 displays the typical Raman spectrum of the samples after laser annealing, without further thermal treatment. For comparison, the Raman spectra of the as-deposited Ti/Si sample, together with the RTA C54 and C49 $TiSi_2$ are also shown. The as-deposited sample has a weak Raman peak at 137 $cm^{-1}$, due to the first-order transverse optical mode of the Ti film,[14] which disappears in the Raman spectrum of the laser-annealed sample and three new peaks at 193, 201, and 242 $cm^{-1}$ are observed instead, all of which can be assigned to the C54 $TiSi_2$.[5] Our Raman results confirm the formation of C54 phase with laser irradiation.

The high-resolution cross-sectional TEM micrograph shown in Fig. 2 exhibits a typical C54 $TiSi_2$ lattice. It is obvious that the stoichiometry is very uniform across the film. The image also shows that the $TiSi_2$/*c*-Si interface is very sharp and smooth, and the transitional region is only a few atomic layers. The thickness of the films measured by TEM and AFM ranges between 13 and 42 nm with the scanning speed between 1 and 0.1 mm/s (corresponding to exposure times of 0.25 and 2.5 ms, respectively). The elemental compositions of the layers shown in Fig. 2 are characterized using an energy-dispersive spectrometer (EDS) attached to the HRTEM system with the electron beam of 1 nm in diameter and the results are presented in Fig. 3. Calculations using the EDS data and theoretical *k* values can clearly identify the layers shown in Fig. 2 as unreacted Ti, $TiSi_{2.06}$, and Si substrates. The EDS data are in good agreement with the Raman spectroscopy results.

The laser-induced C54 $TiSi_2$ grain size is analyzed by AFM. The samples were carefully etched using an $NH_4OH:H_2O_2:H_2O = 1:1:5$ solution prior to the measurements to completely remove unreacted Ti. Figure 4 shows the AFM micrographs of the typical laser annealed and RTA samples. The average grain size extracted from the AFM micrographs is 85 nm for laser-induced samples and 110 nm for RTA samples.

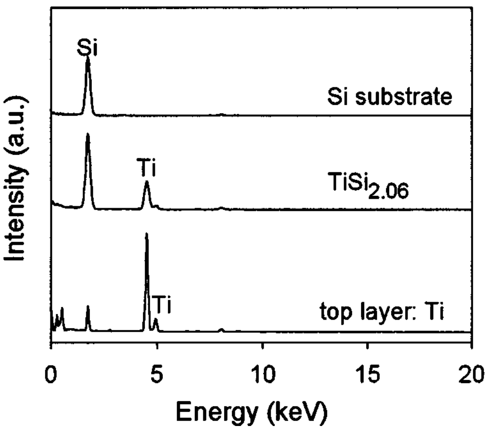

FIG. 3. EDS spectra of the layers shown in Fig. 2. The composition of the layers can be identified as (bottom) unreacted Ti with a small amount of Si, (middle) $TiSi_{2.06}$, and (top) Si substrate.

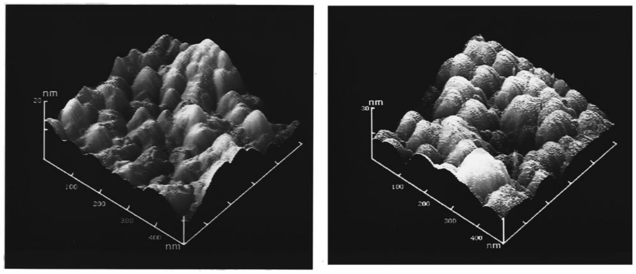

FIG. 4. AFM image of the C54 $TiSi_2$ phase produced by laser annealing (left) and RTA (right), the average grain size is measured to be 85 and 110 nm, respectively.

We have performed computer simulation on the temporal distributions of temperature during laser irradiation. The maximum temperature at the Ti–Si interface is about 1100 °C during laser treatment, which is well below the melting points of Ti (1660 °C) and Si (1412 °C). The results indicate that the solid-state process is responsible for the C54 $TiSi_2$ formation in our experiments rather than melting. The extremely fast ramping rate and the short duration of the laser pulses, together with the fact that the samples do not melt, make it possible to form fine grains and the atomic-scale smooth interface. In this case, the short duration of the pulses limits the growth of silicide grains.

The reaction kinetics has been examined in our experiments. For the reaction-limited (RL) film formation process, the film thickness is proportional to the annealing time, while it is proportional to the square root of the annealing time for the diffusion-limited (DL) process. In our experiments, the film thickness is expected to be inversely proportional, respectively, to the scanning speed and to its square root for the two cases. In Fig. 5 the solid line is a least square fit (LSF) of the experimental data with the imposed condition that the fitted line goes through the origin. The dashed line is the result calculated from the diffusion-limited formation using the preexponential factor $U_0 = 29\,\text{cm}^2/\text{s}$ and activation energy $E_a = 1.8\,\text{eV}$.[15] In this calculation, the film thickness formed by one pulse was obtained by integrating the temperature profile, which is obtained by computer simulation. The calculated result is very close to the experimental data, considering the fact that there are no adjustable parameters in the calculation.

We have also attempted to fit the experimental data using the reaction-limited model. As there are no data on $U_0$ and $E_a$ available for $TiSi_2$ in the reaction-limited case, we have simply fitted the experimental data to a linear function of time, which also has to go through the origin. The fitted result is also plotted in Fig. 5 as the dotted line. Our results clearly favor the diffusion-limited mechanism.

It has to be pointed out here that the laser-annealed samples contain cracks of 1–10 $\mu$m spacing, which leads to the unreliability of the electrical measurement data (not shown). There are two types of stresses which may be responsible for the cracks:[16] (1) the intrinsic stress due to the 26% shrink in volume after silicidation, which induces stresses with the substrate and with the surrounding unsilicided area; and (2) the extrinsic stress caused by the difference in the thermal expansion coefficients between silicide (12.5 ppm/°C) and Si (3 ppm/°C). The elimination of the cracks induced by the laser annealing will be a giant step toward the realization of its application in semiconductor manufacturing.

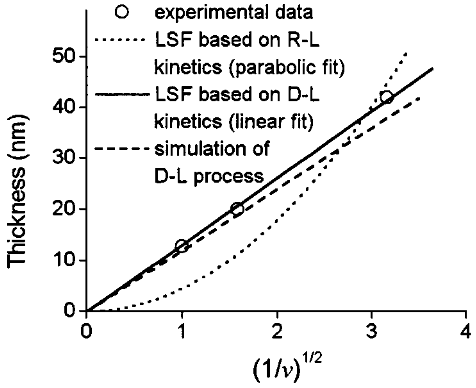

FIG. 5. Scanning speed (mm/s) dependence of silicide thickness.

In summary, direct formation of C54 $TiSi_2$ has been achieved with a *Q*-switched Nd:YAG laser, using industrial standard Ti/Si samples without preamorphization of the *c*-Si substrate, via a solid-state diffusion mechanism. The C54 $TiSi_2$ films formed are single phased and thin, with fine grains and a smooth film/substrate interface on the atomic scale. Laser-induced formation of titanium silicide and other materials may find applications in the subquarter micron technology.

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