Structural study of refractory-metal-free C40 TiSi2 and its transformation to C54 TiSi2

Citation: Applied Physics Letters 80, 2266 (2002); doi: 10.1063/1.1466521
View online: http://dx.doi.org/10.1063/1.1466521
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/80/13?ver=pdfcov
Published by the AIP Publishing

Re-register for Table of Content Alerts
Create a profile. Sign up today!
Structural study of refractory-metal-free C40 TiSi2 and its transformation to C54 TiSi2

T. Yu, a) S. C. Tan, Z. X. Shen, L. W. Chen, and J. Y. Lin

Physics Department, 2 Science Drive 3, Faculty of Science, National University of Singapore,
Singapore 117542

A. K. See
Chartered Semiconductor Manufacturing Limited, 60 Woodlands Industrial Park D. Street 2,
Singapore 738406, Republic of Singapore

(Received 13 November 2001; accepted for publication 1 February 2002)

The formation of C54 TiSi2 has attracted a great deal of attention owing to its significant technological importance in the self-aligned silicide (salicide) processes in ultra-large-scale integration. In a typical salicide process in semiconductor device fabrication, a layer of silicide thin film is formed by reaction between the deposited metal Ti and Si surfaces on gate, source, and drain areas during rapid thermal processing (RTP). As is well known, C49 TiSi2, a metastable phase of TiSi2 with high resistivity of 60–90 μΩ m was usually observed before the formation of C54 TiSi2, which has low resistivity (~15 μΩ m) and high thermal stability. However, this C49–C54 TiSi2 phase transformation becomes very difficult and incomplete for subquarter micron devices due to the lack of sufficient C49 TiSi2 triple-grain boundaries where C54 TiSi2 nucleate.

Recently, significant breakthroughs were reported in which the C54 phase was epitaxially formed from a metastable C40 phase bypassing the C49 phase. Mann et al., Kittl, Gribelyuk, and Samavedam observed that the C40 phase acts as a template allowing the direct formation of the C54 phase and blocking the formation of the C49 phase when a small amount of Mo ions were implanted into the Si substrate prior to Ti film deposition. Another method of forming C40 TiSi2 is by depositing a thin Mo layer of 1 nm in thickness between the Ti film and Si substrate as demonstrated by Mouroux et al. However, as Chen et al. discussed, the use of refractory metals also raised several important issues. More recently, the refractory-metal-free C40 TiSi2 was synthesized by Chen et al. using a laser-annealing process and identified by Li, Chen, and Shen using convergent beam electron diffraction (CBED) and CBED pattern simulation. In their work, the formation of C40 TiSi2 was attributed to kinetic factors resulting from the extreme thermal nonequilibrium induced by the pulsed laser annealing.

As a new TiSi2 phase, the crystal structure of C40 TiSi2 has been systematically investigated by high-resolution transmission electron microscopy (HRTEM), and the direct phase transformation from the C40 phase to C54 phase was studied by Raman spectroscopy. However, the pure C40–C54 transformation bypassing the C49 TiSi2 phase has never been studied by x-ray diffraction (XRD), even the XRD pattern of the pure C40 phase resulting from the refractor-metal-free Ti/Si samples. In this work, we used x-ray diffraction to characterize C40 TiSi2 directly formed by pulsed laser annealing a pure Ti/Si sample and the C40–C54 TiSi2 phase transformation upon further RTP annealing.

The preparation of precursor Ti/Si samples and the pulsed laser annealing process has been reported in detail by Chen et al. and Li, Chen, and Shen. A Digital Instruments (Dimension™ 3000 SPM) atomic-force microscope (AFM) with tapping mode was used to demonstrate the morphology and average grain size of pure C40 TiSi2 induced by laser annealing. A RTP processor (Jipelec JetFirst system) was employed to transform pure C40 TiSi2 to C54 TiSi2 by heating the samples at different temperatures for 60 s. The samples after various temperature RTP treatments were identified by a SPEX 1702/04 micro-Raman spectrometer with a He–Ne laser (λ = 632.8 nm) as the excitation source.

Figure 1(a) shows the typical top-view AFM image of the laser-irradiated sample after etching in NH4 OH:H2O2:H2O = 1:1:6 for complete removal of the unreacted surface Ti film. As shown, the average grain size is about 50 nm with a high uniformity of grain size and distribution.

Figure 1(b) (bottom spectrum) displays the Raman modes of the same as-laser-annealed sample. Compared with the previous results, it is obvious that pure C40 TiSi2 is the dominant phase after the laser annealing process in this work.

The crystal structure of C40 TiSi2 has been identified using HRTEM by Li, Chen, and Shen and normal Bragg–Bentano XRD by Via et al. By using glancing-angle XRD

a)Author to whom correspondence should be addressed; electronic mail: scip96000@nus.edu.sg

DOI: 10.1063/1.1466521

APPLIED PHYSICS LETTERS VOLUME 80, NUMBER 13 1 APRIL 2002

22660003-6951/2002/80(13)/2266/3/$19.00 © 2002 American Institute of Physics

0003-6951/2002/80(13)/2266/3/$19.00 © 2002 American Institute of Physics
effectively multiply the x-ray diffraction by the surface TiSi$_2$
comparison, the XRD peak positions for the Ti$_{0.4}$Mo$_{0.6}$Si$_2$
 five peaks at 37.96°, 40.43°, 41.04°, 43.92°, and 47.24°. For
tom curve
diffracted x-ray during the scan. As shown in Fig. 2
sample surface while the detector was rotated to collect the
free C40 TiSi$_2$ and C40–C54 phase transformations were
It is obvious that the XRD peaks of laser-induced refractory-
positions of laser-induced C40 TiSi$_2$ are quite close to that of
TaSi$_2$. This can be explained as the small difference in lattice
parameters between C40 TiSi$_2$ and TaSi$_2$ as reported by
Via et al. It is noted that the results of Li, Chen, and Shen have
shown that pure C40 TiSi$_2$ has a hexagonal structure (P6$_2$22).
Therefore, we set the XRD pattern shown in Fig.
2(b) (bottom) as the hexagonal structure with space group
P6$_2$22. After addressing the five peaks to the (110), (111),
(003), (200), and (112) planes of C40 TiSi$_2$, we obtained the
experimental lattice parameters ($a$ = 0.467 nm, $c$ = 0.662 nm)
of pure C40 TiSi$_2$. It is well matched with the HRTEM
results ($a$ = 0.471 nm, $c$ = 0.653 nm), and BBXRD results
($a$ = 0.469 nm, $c$ = 0.649 nm). Our experimental results
for the interplanar distance, 2.19 Å for the (003) plane, 2.23 Å
for the (111) plane, and 1.92 Å for the (112) plane, also show
excellent agreement with the HRTEM results of 2.18, 2.21,
and 1.92 Å, respectively.

In order to study the phase transformation from C40
TiSi$_2$ to C54 TiSi$_2$, we used RTP to anneal the laser-induced
C40 TiSi$_2$ sample at various temperatures for the same duration
(60 s). Figure 2(b) illustrates the GAXRD patterns of C40 TiSi$_2$ after annealing at different temperatures. As
shown, the C54 phase appears after a relative low
temperature ($T$ = 630 °C) RTP treatment. Interestingly, the
peak intensity of XRD peaks belonging to C40 TiSi$_2$
increases dramatically with a large reduction of the full width
at half maximum (FWHM), even after the appearance of the
C54 phase. By considering the typical x-ray diffraction
theory, it is quite reasonable to attribute this phenomenon to

(GAXRD) operating under the detector scan mode to analyze
the samples instead of the common Bragg–Bentano XRD
(BBXRD) method, which operates at the $\theta$–2$\theta$ mode, we can
effectively multiply the x-ray diffraction by the surface TiSi$_2$
thin film and strongly reduce the penetration depth and
collection time. The crystal structure of the refractory-metal-
free C40 TiSi$_2$ and C40–C54 phase transformations were
studied by GAXRD at room temperature. In this work, XRD
patterns were taken using a D8 ADVANCE x-ray diffracto-
ometry (Bruker Analytical X-Ray Systems). A Cu K$_\alpha$
source ($\lambda$ = 1.5406 Å) was used at 40 kV and 40 mA. The
GAXRD diffraction geometry is shown schematically in Fig.
2(a). The incidence angle $\alpha$ was fixed at 2° relative to the
sample surface while the detector was rotated to collect the
diffracted x-ray during the scan. As shown in Fig. 2(b) (bottom
curve), the GAXRD pattern of pure C40 TiSi$_2$ presents
five peaks at 37.96°, 40.43°, 41.04°, 43.92°, and 47.24°. For
comparison, the XRD peak positions for the Ti$_{0.4}$Mo$_{0.6}$Si$_2$
(Ref. 14a) ($a$ = 0.465 nm, $c$ = 0.650 nm), Ti$_{0.8}$Mo$_{0.2}$Si$_2$
(Ref. 14b) ($a$ = 0.470 nm, $c$ = 0.652 nm), and TaSi$_2$
(Ref. 14c) ($a$ = 0.478 nm, $c$ = 0.657 nm) were also indicated in Fig. 2(b).
It is obvious that the XRD peaks of laser-induced refractory-
metal-free C40 TiSi$_2$ match well with the other well-known
C40 phase silicides, all of which have the hexagonal crystal
structure with space group P6$_2$22 (180). Especially, the peak
positions of laser-induced C40 TiSi$_2$ are quite close to that of

FIG. 1. (a) AFM image of the TiSi$_2$ C40 phase produced by laser anneal of
the Ti/Si sample. (b) Raman spectra of the C40 phase before and after RTP
treatments.

FIG. 2. (a) Schematic diagram of the GAXRD geometry, incidence angle $\alpha$
of the x-ray is fixed at 2° and the detector is scanned during experiment. (b) XRD patterns of the as-laser-annealed C40 TiSi$_2$ sample before and after RTP
treatments.
the ordering and perfecting process of crystalline C40 TiSi2 caused by low-temperature RTP annealing. Notice that the coexistence of the more-ordered C40 phase, and the C54 phase is strongly related to the epitaxial growth behavior between C40 TiSi2 and C54 TiSi2. With the increase in temperature, the dominant phase transforms from the C40 TiSi2 before RTP to the C54 TiSi2 after RTP at 660°C for 60 s. Further annealing (T=700°C) completely transforms C40 TiSi2 to C54 TiSi2, characterized by the XRD pattern of the pure C54 TiSi2 phase.15 Our XRD results indicate that C49 TiSi2 is never formed for all RTP treated (T=625–700°C) laser-induced C40 TiSi2 samples. Hence, the laser-induced refractory-metal-free C40 TiSi2 can greatly decrease the C54 TiSi2 formation temperature and directly transform to C54TiSi2, completely bypassing the C49 TiSi2.

Figure 1(b) also shows the Raman spectra of the samples corresponding to the GAXRD patterns shown in Fig. 2(b), which strongly support the conclusions drawn from the XRD study that the laser-induced refractory-metal-free C40 TiSi2 can directly transform to C54 TiSi2, bypassing the C49 phase. A detailed Raman study has been presented by Chen et al.10 that demonstrated the same result. Similar to the XRD peaks, the Raman peaks of the C40 phase also display a dramatic increase of intensity and decrease of FWHM. Peak splitting at around 280 cm−1 is clearly seen in the 630°C annealed spectrum, corresponding to a more-ordered C40 TiSi2 phase. More interestingly, an obvious blueshift of the C40 TiSi2 vibrational modes occurs with increasing RTP temperature while a slight redshift of the C54 TiSi2 vibrational modes can be observed with further annealing. The Raman mode shifts most likely result from stress, which is mainly caused by the mismatch between the substrate Si and the C40 TiSi2 as well as between C40 and C54 TiSi2. Raman modes are very sensitive to stress, and different kinds of stress (compress or tensile) induce contrast shifts (blueshift or redshift)16 in the Raman spectra.

In conclusion, the structure of laser-induced refractory-metal-free C40 TiSi2 has been studied using GAXRD. Both GAXRD and the Raman study unambiguously demonstrate that this laser-induced C40 TiSi2 can directly transform to C54 TiSi2 at a relatively low temperature.

References