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H. Westberg, M. Boman, J.-O. Carlsson. Laser-assisted chemical vapour deposition of TiSi₂: aspects of deposition and etching. Journal de Physique IV Proceedings, 1993, 03 (C3), pp.C3-225-C3-232. 10.1051/jp4:1993330 . jpa-00251387

HAL Id: jpa-00251387

<https://hal.science/jpa-00251387>

Submitted on 1 Jan 1993

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Laser-assisted chemical vapour deposition of TiSi_2 : aspects of deposition and etching

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ABSTRACT

Lines of TiSi_2 were written on Si(100) substrates by using a focused Ar^+ -laser. The reaction gas mixture consisted of TiCl_4 and H_2 and the substrate was used as the silicon source. The laser deposited TiSi_2 lines were examined as a function of the deposition parameters. Especially the initial reactions have been studied by varying the writing speed in a wide range. The C-54 phase of TiSi_2 was observed in all experiments. The geometrical shape and the surface profile of the deposited TiSi_2 were complicated functions of the process parameters and the growth process itself. Substrate reactions increased the substrate etching initially. After a sufficiently thick layer of TiSi_2 had been grown, thus protecting the substrate from the reaction gas mixture, the etch process stopped. By minimizing the initial substrate reactions, flat lines with respect to the substrate surface could be grown.

1 INTRODUCTION

TiSi_2 is of interest as a gate electrode and an interconnect material in VLSI circuits because of its low resistivity and good compatibility with standard IC processing techniques. For these applications it is important that the substrate surface remains relatively flat during the deposition process. The molar volume difference between Si and TiSi_2 is only 7%. Thus by using the substrate as the silicon source and an external titanium source (e.g. from the vapor) relatively flat TiSi_2 lines can be grown [1]. In this paper we have used thermal laser assisted chemical vapor deposition (LCVD) to grow TiSi_2 lines on a silicon substrate.

LCVD using a focused laser beam perpendicular to the substrate surface is a very complex process. This is partly because of a gaussian intensity distribution of the laser beam which generates a temperature gradient across the spot on the substrate or on the deposited material. The temperature gradient may alter the chemistry over the laser processed spot resulting in differences in the phase composition and/or chemical composition.

Generally the deposition time in LCVD is very short. This means that the initial reactions will dominate the deposition process. Initially the substrate is exposed to the reaction gas mixture. If the substrate is chemically reactive towards the gas phase, substrate etching will occur with the formation of gaseous substrate compounds. Later on, when the deposited material has protected the substrate surface from the reaction gas mixture, the etch reaction will be slower. Occurrence of such initial etch reactions may influence

- the adhesion. If an etching process occurs it might result in a corrosion attack on the substrate, yielding poor adhesion of the laser deposited material.
- chemical and phase composition of the laser deposited material. Gaseous substrate compounds may after transport in the vapour, be redeposited at a substrate location having a lower activity with respect to the transported substrate element than the location where the reactive evaporation took place.

- the deposition rate and grain size of the laser deposited material. The etch reaction often increases the driving force of the CVD process and hence the deposition rate. This may result in a more fine-grained deposit near the substrate/coating interface. Subsequently in the process, when the substrate is not exposed to the vapour, a larger-grained deposit may be expected.

Depending on the scanning velocity the relative influence of the initial reactions, e.g. substrate etching, on the process will be different. For a high scanning velocity, i.e., a short deposition time, the etch reaction may dominate the deposition process entirely.

TiSi₂-lines were deposited from a reaction between the substrate silicon and a gas mixture consisting of TiCl₄ and H₂. This deposition process can be described approximately by the overall reactions,

In reaction (1) the TiCl₄ is reduced by the silicon substrate and in the second reaction TiCl₄ is reduced by hydrogen. This means that either SiH₃Cl or HCl are formed in addition to TiSi₂. However, there are several other possible reaction pathways where different gaseous chlorosilanes, SiH_xCl_{4-x} (0 ≤ x ≤ 4), are formed. The reaction pathway depends mainly on the H₂/TiCl₄ molar ratio and the deposition temperature. Since the silicon substrate is reactive towards the gas phase etching of the substrate will take place.

A considerable substrate etching under the laser deposited lines was earlier observed in LCVD of TiSi₂ [1]. Frequently a larger etching was found along the edges than in the centre of the line. This means that the surface profiles perpendicular to the laser-written lines were bimodal in shape.

In the present investigation the deposition conditions have been varied in wide ranges to study the effect on the surface profile, the growth kinetics and the morphologies. The importance of the deposition time was especially examined. TiSi₂ has previously been deposited by thermally activated CVD, plasma-activated CVD and also laser-induced CVD[1-7].

2 EXPERIMENTAL

The laser system is schematically shown in Figure 1. Details of the system have been presented elsewhere [8] and only a brief description is given here.

Fig. 1. Sketch of the LCVD system

A cw Argon ion laser, Innova 100 UVE+, was operated at a wavelength of 514.5 nm. The gaussian beam shape was used throughout the experiments. The laser beam was at perpendicular incidence and focused through a quartz window onto the substrate. The spot diameter was measured to be, $2\omega_0 = 21 \mu\text{m}$, ($1/e^2$ decrease in intensity) according to the scanning knife edge method [9]. The laser speckle method was used to get the substrate in the focal plane. For the direct writing, the reaction chamber

and the focusing lens were placed on computer controlled high resolution x-y-z stages with a mechanical resolution of 4 nm, an accuracy of 0.5 μm and a speed range of 4 nm/s - 4 mm/s. The laser power was continuously measured during the deposition experiments.

The experiments were performed in an open cold wall CVD reactor. A gas handling system and an evaporator for TiCl_4 were used to provide the reactor with the reaction gas mixture. For control of the total pressure an automatic pressure controller was employed.

2.1 Deposition conditions

Silicon (100) (P doped, resistivity 10 Ωcm) wafers were used as substrates. The gaseous reactants, H_2 and TiCl_4 , had a purity of 99.9997% and 99.995%, respectively. For the TiSi_2 growth the substrate was used as the silicon source.

Prior to the deposition experiments, the substrates were cleaned by first oxidizing in an $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ mixture for 10 minutes at 95°C and then etching in HF (10%) for 10 seconds. This cleaning procedure yields a hydrogen terminated surface. The substrate will remain hydrogenated even after transport in the atmosphere and only small amounts of oxygen on the surface can be seen. Hydrogen is desorbed in the LCVD process when the temperature has increased to about 400 ° [10], leaving a clean silicon surface exposed to the reaction gas mixture. After the deposition, the subchlorides, which condensed just outside the heated region, were removed by a dip in 2 M hydrochloric acid for a few seconds. The laser power density and the scanning velocity were varied in the range 6.8 - 8.5 $\cdot 10^5$ W/cm² and 1.0 - 600.0 $\mu\text{m/s}$, respectively. The H_2/TiCl_4 molar ratio was varied in the range 900/1 to 900/9.

2.2 Characterization

Phase analysis and texture investigation were performed by X-ray diffractometry (XRD) using a powder diffractometer with CuK_α radiation. The chemical composition was determined by Auger Electron Spectroscopy (AES). The morphology and the microstructure were investigated by scanning electron microscopy (SEM).

To obtain the film thickness, cross-sections of the deposited lines were measured from SEM micrographs. For the preparation of the cross-sections, glueing of specimen to another silicon wafer was used. This procedure reduces the degradation of the surfaces, including the lines, during the polishing. By sequential polishing, several cross-sections could be measured from each line. The substrate etching and profile of the line perpendicular to the scanning direction were examined by a profilometer (depth resolution 50 Å). The substrate etching was defined as the distance between the substrate surface and the TiSi_2 deposit in the centre of the laser deposited line.

2.3 Temperature determination

Temperature measurements are very difficult to perform in focused beam LCVD since the heated area is small and since the temperature varies across the laser spot on the substrate surface. However, the temperature can be calculated if the thermal conductivity and the reflectivity of the substrate and the deposit are known as a function of temperature. For a presentation of the temperature calculation technique and the thermal constants used in LCVD of TiSi_2 , see ref. [1]. Throughout this paper, both the laser power density and the highest laser induced temperature refer to the centre of the laser spot. This temperature was calculated for silicon [1], i.e., the laser induced temperature prior to any deposition of TiSi_2 .

3 RESULTS

3.1 Surface profiles

Figure 2 shows the surface profiles (obtained from profilometer measurements) as a function of inverse scanning velocity. Since the inverse scanning velocity is proportional to the deposition time, the figures show the thickness of the TiSi_2 lines as a function of time and represent different stages of growth. The deposited TiSi_2 region, also showed in Fig. 2, is dashed and has been drawn from SEM cross-sections.

Etching of the silicon substrate could only be avoided for TiSi_2 lines deposited at scanning velocities exceeding 600 $\mu\text{m/s}$ (1.7 ms/ μm). However, no deposition or only a few scattered nuclei of TiSi_2 were observed at such short deposition times. The small increase in thickness shown in Figure 2a represents the surface profile of the line deposited at 300 $\mu\text{m/s}$. The deposit is slightly elevated in the centre of the line. This indicates a low etch rate of the substrate.

Fig. 2. *Morphology and surface profiles of laser deposited TiSi_2 lines as a function of scanning velocity. Laser power density: $7.74 \cdot 10^5 \text{ W/cm}^2$ (1460 K). Molar ratio H_2/TiCl_4 : 900/1.*

Fig. 3. *Morphology and surface profiles of laser deposited TiSi_2 lines as a function of laser power density. Scanning velocity: $10 \mu\text{m/s}$. Molar ratio H_2/TiCl_4 : 900/1.*

Fig 2b shows the surface profile of a line deposited at a lower scanning velocity (80 $\mu\text{m/s}$). This surface profile shows that the substrate has been slightly etched in the centre and that the deposit is elevated above the surface level along the edges. This type of surface profile is frequently observed in laser melted materials structures.

At a somewhat longer deposition time (100 ms/ μm), at a scanning velocity of 10 $\mu\text{m/s}$, the elevation along the edges of the line has been suppressed and the surface profile is concave with a maximum etch depth of 0.4 μm , see Fig 2c. At the longest deposition time examined (1.0 s/ μm), the largest etch depth (about 0.5 μm) was found along the edges of the line. In the centre of the line the etch depth was considerably smaller and a bimodal surface profile was obtained.

Fig 3 a-c shows the surface profiles of laser deposited TiSi_2 as a function of the laser power density. Increasing the laser power density from $6.2 \cdot 10^5 \text{ W/cm}^2$ (1180 K) to $7.9 \cdot 10^5 \text{ W/cm}^2$ (1490 K) means that the etch depth in the centre of the laser processed area will increase from 0.04 μm to about 0.4 μm . On both sides and at distances 5 and 15 μm of the etch groove the etch rate is lower and the deposit is slightly above the surface, see Fig 3b and 3c. The surface profile in Fig. 3c indicates surface melting of the deposited TiSi_2 .

3.2 Morphology and microstructure

Figure 2 a-d shows the morphology of the laser deposited TiSi_2 lines as a function of scanning velocity. The initial stage of growth is represented by the fastest scanning velocity used, 600.0 $\mu\text{m/s}$ (1.67 ms/ μm), not shown in Fig. 2. The silicon substrate was affected in an irregular manner and a random nucleation of TiSi_2 was observed. At a somewhat longer deposition time, at a scanning velocity of 300.0 $\mu\text{m/s}$ (3.3 ms/ μm), periodic surface structures started to appear in the centre of the laser heated region (Fig. 2 a). The surface structure, so called ripples, had a spacing of approximately 0.4 μm . This is slightly shorter than the wavelength used (0.514 μm). The ripples run normal to the electric field vector of the incident polarized laser beam. A rippled morphology of the deposited TiSi_2 was observed for all scanning velocities except at 1 $\mu\text{m/s}$ where a relative thick film of 2.5 μm had developed. At this scanning velocity the deposit was rough and porous. Whiskers were also frequently observed.

The laser power density, i.e. the temperature, strongly influenced the morphology of the laser deposited TiSi_2 lines, see Fig. 3. The morphology of the line deposited at the lowest laser power density, $6.2 \cdot 10^5 \text{ W/cm}^2$ (1180 K), was fine-grained, smooth and free from pores and cracks (Fig. 3a). The line was thin, 5.4 μm wide, but well defined along the edges. Cracks and pores appeared in the centre of the deposit when the laser power density was increased. This is seen in figure 3 b which shows a line deposited at $7.2 \cdot 10^5 \text{ W/cm}^2$ (1380 K). At this laser power density a periodic surface structure was observed. Increasing the laser power density to $7.9 \cdot 10^5 \text{ W/cm}^2$ (1490 K), resulted in a much more developed periodic surface structure, see Fig. 3c.

The best quality TiSi_2 with respect to smoothness and porosity was obtained at scanning velocities of at least 20 $\mu\text{m/s}$ and at laser power densities ranging from about $6.2 \cdot 10^5$ (1180 K) to $7.2 \cdot 10^5 \text{ W/cm}^2$ (1380 K). In this range, the scanning velocity is high enough to avoid whisker-like growth and the laser power density is sufficiently low to avoid formation of cracks and a rippled surface structure. A higher linear gas flow velocity further improved the quality of the deposit. A more fine-grained and smoother morphology was obtained and whisker-like growth was suppressed. When the total pressure was increased ten times to 75 torr, the deposition rate increased several times. The lines were no longer embedded in the silicon substrate but elevated from it. The morphology was in most cases very porous and the grain size was small (0.1 - 0.2 μm).

3.3 Chemical and phase composition

X-ray diffraction showed that the laser deposited material contained the orthorhombic C-54 modification of TiSi_2 having a (001) texture.

The AES analysis showed that the composition of the laser deposited lines was close to TiSi_2 , except for lines deposited for long times (1 μm and 2 $\mu\text{m/s}$) where an excess of titanium was observed with respect to TiSi_2 . All the TiSi_2 lines contained a large amount of oxygen even after sputtering prior to the analysis. TiSi_2 is known to oxidize very fast in the air and a mixed titanium-silicon oxide is formed. No chlorine was observed in the spectra.

The granular structure found initially (at 1.7 ms/ μm) on the silicon surface, i.e., at the highest scanning velocity, consisted mainly of titanium oxide (TiO_x). The rippled surface structure contained a lower content of titanium and also a higher content of silicon than the granular structure. This indicated that the silicide formation had started and that the rippled structure appeared in connection with this. The titanium and also the silicon content was found to vary across the line. In the centre of the line

and of the surface structure, the titanium content was lower and the amount of silicon was higher than along the edges. This tendency is enhanced for lines deposited at higher laser power densities, when the rippled structure is more developed.

3.4 Kinetics

In this section, the dependence of film thickness and etch depth is presented as a function of process parameters. Both the film thickness and the etch depth, which are shown in the following figures, were measured in the centre of the lines.

Neither the film thickness nor the etch depth were influenced by the linear gas flow velocities in the range 2 - 176 cm/s. This indicates that the process is surface reaction controlled.

Fig. 4. Etch depth (a) and thickness of TiSi_2 (b) as a function of the inverse scanning velocity. Laser power density: $7.6 \cdot 10^5 \text{ W/cm}^2$ (1450 K). Molar ratio H_2/TiCl_4 : 900/1

Fig. 5. Etch depth (a) and thickness of TiSi_2 (b) as a function of the laser power density. Scanning velocity: $10 \mu\text{m/s}$. Molar ratio H_2/TiCl_4 : 900/1.

Figure 4 shows the film thickness and etched depth as a function of inverse scanning velocity. Bimodal surface profiles were obtained for the lines deposited at 1.0 and $2.0 \mu\text{m/s}$. The film thickness increased linearly, from 0.26 to $2.5 \mu\text{m}$, with increasing deposition time. Initially, the etch depth increased very fast with increasing inverse scanning velocity and at about $0.2 \mu\text{m/s}$ a maximum in etch depth, $0.45 \mu\text{m}$, was obtained. For higher inverse scanning velocities the etch depth decreased and was at $1 \text{ s}/\mu\text{m}$ $0.1 \mu\text{m}$. Both the film thickness and the etch depth were found to increase linearly with increasing laser power density, see Fig. 5. The film thickness increased from 0.34 to $0.65 \mu\text{m}$ and the etched depth from 0.16 to $0.60 \mu\text{m}$ between $6.8 \cdot 10^5$ (1300 K) and $8.3 \cdot 10^5 \text{ W/cm}^2$ (1520 K).

In order to gain some insight in the type of process controll, data from Fig. 5 was plotted in an Arrhenius diagram and a rough estimate of the apparent activation energy AAE could be made, see Fig. 6. The laser power density was converted to temperature by using the calculated laser induced temperature on a silicon substrate, i.e., representing initial conditions prior to any deposition of TiSi_2 . The (AAE) for both deposition and etching was found to be low, about 45 kJ/mol and 90 kJ/mol , respectively.

Fig. 7 shows the influence of the TiCl_4 -concentration on the deposition and etch rate. The film thickness increases linearly with the TiCl_4 -concentration up to 0.6% irrespective of the scanning velocity. The film thickness decreased between 0.6 and 1% TiCl_4 in the gas phase and for 2 and $5 \mu\text{m/s}$ in scanning velocity. Also the etched depth increased linearly with increasing TiCl_4 concentration for lines deposited at scanning velocities of 5.0 and $10.0 \mu\text{m/s}$. Another dependence was obtained for the lowest scanning velocity, $2.0 \mu\text{m/s}$. After a slow increase in the etch depth up to about 0.6% TiCl_4 the increase accelerates towards the highest TiCl_4 -concentration. The high increase in etch rate at this high TiCl_4 -concentration was followed by a decrease in the deposition rate.

Fig. 6. Etch depth (a) and film thickness (b) represented in Arrhenius' curves. Scanning velocity: $10 \mu\text{m/s}$. Molar ratio H_2/TiCl_4 : 900/1.

Fig. 7. Etch depth (a) and thickness of the TiSi_2 deposit (b) as a function of molar ratio H_2/TiCl_4 . Scanning velocity: $10 \mu\text{m/s}$. Laser power density: $7.6 \cdot 10^6 \text{ W/cm}^2$ (1450 K).

4 DISCUSSION

The threshold temperature for the silicide formation between Si and a thin layer of Ti is reported to be about 800 K [11]. However, initial interfacial reactions which involves titanium-silicon intermixing has been observed at lower temperatures, about 570 K [11]. The growth of the silicide from Si and Ti shows a parabolic behaviour which indicates that the process is limited by a transport through the silicide layer. The activation energy of this diffusion reaction is reported to be 1.8 eV (170 kJ/mol) [12].

An LCVD process where TiSi_2 is formed from $\text{TiCl}_4/\text{H}_2/\text{Si}$ is more complicated and can be controlled by mass transport in the vapour, surface kinetics and/or solid state diffusion. If the deposition time is short the process can also be controlled by the nucleation. Since the chemical processes responsible for film growth varies with the film thickness, different types of process control may be present at different stages of growth. Initially the silicon substrate is exposed to the reaction gas mixture. Since Si is a better reducing agent than H_2 towards TiCl_4 the driving force of the process and hence the reaction rate may be high initially, after nucleation. This may result in a mass transport controlled process. Later on when the substrate is separated from the vapour by the growing TiSi_2 , the growth rate decreases and the process becomes surface kinetically controlled. When a thick layer of TiSi_2 has been grown, the diffusion resistance of Si through TiSi_2 becomes higher and the process will be controlled by the solid state diffusion of Si.

At the shortest deposition times (highest scanning velocities 600 and 300 $\mu\text{m/s}$) LCVD of TiSi_2 from $\text{TiCl}_4/\text{H}_2/\text{Si}$ was probably limited by nucleation. For longer deposition times a low activation energy (45 kJ/mol) indicated a mass transport controlled process. However, a mass transport controlled process is sensitive to variations in the linear gas flow velocity. This was not verified by the experiments. On the contrary the film thickness was independent on the linear gas flow velocity. The linear dependence of the film thickness as a function of deposition time excludes a solid state diffusion controlled process which has a parabolic dependence. The most probable type of control is therefore surface kinetics having a low AAE.

The geometrical shape and the surface profile of the deposited TiSi_2 is a complicated function of the process parameters and the growth process itself. The rapid increase in etch rate with increasing deposition time (up to 0.2 s/ μm) as shown in Fig. 4, can be explained by the fact that the substrate is exposed to the reaction gas mixture and reaction (1) dominates. When the substrate becomes completely covered by TiSi_2 the etch process stops at deposition times longer than 0.2 s/ μm . This reflects the fact that reaction (2) becomes more important. The surface profile as a function of deposition time then

strongly depends on the development and growth of the TiSi_2 -layer, separating the substrate from the reaction gas mixture. At 80 and 10 $\mu\text{m/s}$ (0.0125 and 0.1 $\text{ms}/\mu\text{m}$, respectively) the etch depth is highest in the centre of the deposited line, see Fig. 2. For even longer deposition times the TiSi_2 deposit grows thick in the centre of the line. Since the silicon substrate now is effectively separated from the reaction gas mixture, the etch rate is low and reaction (1) is dominating. A low etch rate combined with a volume increase (7%) during growth of TiSi_2 means that the etch depth in the centre of the string will be suppressed resulting in a bimodal surface profile.

The surface profile in Figures 2c, 3b and 3c indicated surface melting of the deposited TiSi_2 at laser power densities lower than expected ($7.7 \cdot 10^5 \text{ W/cm}^2$, $T=1460 \text{ K}$) - the estimated laser induced temperature was lower than the melting point of both Si and TiSi_2 . This was supported by experiments performed in a hydrogen atmosphere in order to study surface melting of silicon. A minimum laser power density of $8.9 \cdot 10^5 \text{ W/cm}^2$ was required to melt the silicon at a scanning velocity $\approx 80 \mu\text{m/s}$ (calculated temperature: 1680 K). In Figures 2c, 3b and 3c a rough and rippled morphology (see below) was observed. This will decrease the reflectivity due to multiple reflection on the TiSi_2 surface and a higher temperature than calculated will result. The lowest possible melting temperature (1600 K) in the Ti-Si system is an eutecticum at 83 at% Si which then must have been exceeded.

Periodic surface structures, so called ripples, were obtained at an early stage of growth at relatively high laser power densities ($7.7 \cdot 10^5 \text{ W/cm}^2$). There have been several attempts to explain the occurrence of the ripples [13]. Generally, it is believed that ripples arise because of an interference effect between incident and scattered light.

Ripples was also observed in the previous paper in LCVD of TiSi_2 [1]. A minimum laser power density of $9.5 \cdot 10^5 \text{ W/cm}^2$ and a low scanning velocity (2 $\mu\text{m/s}$) were then required to produce the ripples. This laser power density corresponds to a temperature which is sufficiently high to melt the TiSi_2 deposit. The laser power density, $7.7 \cdot 10^5 \text{ W/cm}^2$, which was used in this investigation corresponds to a too low calculated temperature to cause surface melting according to the discussion above.

Acknowledgement

The financial support of this project by SECO Tools AB and the Swedish Board for Technical Development is gratefully acknowledged.

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