Laser direct writing of titanium silicide thin films

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Investigations concerning the laser-induced chemical vapour deposition of TiSi$_2$ thin films from SiH$_4$ and TiCl$_4$ using a direct writing method are presented. A CO$_2$-laser at $\lambda = 10.6 \mu$m and an argon ion laser in the VIS (456–527 nm, multiline mode) were used for the preferably thermal deposition on SiO$_2$ and c-Si substrates. The influence of the deposition parameters gas composition, laser power, scan velocity and laser wavelength on structural, geometric, and electrical properties is reported.

1. Introduction

Titanium silicide TiSi$_2$ is because of its low film resistivity of about 25 $\mu$Ω·cm a promising alternative to the doped p-Si in gate electrodes and metallization schemes in integrated circuits as well as in micromechanical and micro-optical devices [1]. The direct writing method as variant of laser-induced chemical vapour deposition offers the advantage of depositing thin film structures with small lateral dimensions without photomasks [2]. The availability of different laser wavelengths allows the use of a variety of source gases on different substrates depending on their optical properties.

We investigated the laser-induced chemical vapour deposition of TiSi$_2$ thin films on silicon and silicon dioxide substrates using a CO$_2$-laser and an argon ion laser. Typical CVD gases like silane SiH$_4$ as silicon source and H$_2$, N$_2$, or Ar as carrier gases were used in combination with titanium tetrachloride TiCl$_4$ as titanium source. Differences between the experimental results in the visible and in the far infrared wavelength range are analyzed and reported here.

2. Experimental

The direct writing experiments were carried out using a stainless steel reaction chamber mounted on a computer-controlled translation stage. The deposition arrangement can be operated in a flow regime. The working pressure was maintained by an oil-sealed fore pump in combination with an oil diffusion pump. The silane flow was measured and adjusted by a flow meter with needle valve. The titanium tetrachloride which is a liquid with a vapour pressure of about 1.33 kPa at room temperature (20°C) was stored in a gas bubbler near the reaction chamber. The TiCl$_4$/H$_2$/SiH$_4$ ratio in the reaction chamber can be varied by controlling the SiH$_4$ gas flow and the H$_2$ gas flow through the bubbler. Thereby, the TiCl$_4$ content has a non-linear dependence on the H$_2$ flow.

The laser beam of a 200 W CW-CO$_2$-laser was focussed onto the surface of a SiO$_2$ substrate resulting in a spot with a Gaussian radius of $r_g = 500 \mu$m. A 3 W argon ion laser ILA 120-1 was used for the deposition on c-Si and oxidized c-Si substrates. Three exchangeable objectives...
producing different spots of \( r_G = 4, 7 \) and 15 \( \mu \text{m} \) were applied. More details concerning the experimental apparatus can be found in ref. [3].

3. \( \text{CO}_2 \)-laser-induced deposition of TiSi\(_2\)

The deposition of TiSi\(_2\) on SiO\(_2\) substrates was carried out using the \( \text{CO}_2 \)-laser on SiO\(_2\) substrates because of the high absorptivity of the substrate at this wavelength. The total pressure of the reactant gas mixture of TiCl\(_4\), SiH\(_4\) and H\(_2\) as carrier gas for the TiCl\(_4\) molecules was held constant at a value of 1.2 kPa. The gas flow ratio between the TiCl\(_4\)·H\(_2\) flow and the SiH\(_4\) flow has been varied between 0.2 and 0.6 in order to study the influence on the film stoichiometry. An increase in the TiCl\(_4\)·H\(_2\)/SiH\(_4\) ratio enhances the Ti content in the films (fig. 1a). This tendency is related to a negative side effect which was observed as an increasing substrate etching caused by the rise of the concentration of chlorine and the lower chlorides of the titanium within and near the deposition zone. The films grow on the substrate material. A RBS depth profile (fig. 1b) shows that the Ti content increases with film thickness. We believe that this effect is due to the inhibited nucleation of TiSi\(_2\) on clean SiO\(_2\) surfaces [4]. Therefore, a first layer of p-Si from SiH\(_4\) is created, followed by an increasing Ti and TiSi\(_2\) incorporation into the growing film.

The dependence of the geometric line profile on the TiCl\(_4\)·H\(_2\)/SiH\(_4\) flow ratio exhibits the strengthening of the etching behaviour with the increasing TiCl\(_4\)·H\(_2\) content within the gas phase (fig. 2) mentioned above.

The film deposition process is self-limiting in thickness in the centre of the lines if the TiCl\(_4\)·H\(_2\)/SiH\(_4\) ratio of 0.6–0.7 is reached. At these values of the TiCl\(_4\)·H\(_2\)/SiH\(_4\) ratio the lowest specific film resistance of 160 \( \mu \Omega \text{cm} \) was measured. Lowering the flow ratio leads to an increase of the film resistivity because of the rising silicon excess in the films. At flow ratios greater than 0.7 the films become more inhomogeneous.
due to local etching and the incorporation of lower chlorides of titanium and silane. Therefore, the film resistivity increases again.

A variation of the scan speed within the range of 0.02–0.2 mm/s showed no influence on the electrical and structural film properties because of the large illumination time of 50–5 s at a spot diameter of about 1 mm. The deposition rate decreased with increasing illumination time, like shown in fig. 3. We suppose that this behaviour is related to the varying temperature within the reaction zone during the film growth. At the beginning of the deposition a high absorption and low thermal conductivity of the SiO₂ substrate lead to a rapid heating of the surface within the illuminated region. After the deposition of the first Si-rich layers the reflectivity increases and the heat conductivity of the growing film, which is

Fig. 3. Dependence of the deposition rate on the local illumination time and the scan velocity (p₀ = 1.2 kPa, I = 400 W/cm², T₀ = 300 K).

Fig. 4. (a) Optical micrograph of TiSi₂ films on SiO₂ substrates (p₀ = 1.2 kPa, v₀ = 0.1 mm/s, T₀ = 300 K, I = 955 W/cm²). (b) Talstep analysis of periodic structures (parameters see fig. 4a).
greater than that of the substrate, results in a lower surface temperature, therefore, the local deposition rate decreases until an equilibrium is reached.

The immediate vicinity of the TiSi$_2$ lines is contaminated with particles. These particles are probably produced by a homogeneous gas-phase reaction initiated by the absorption of the CO$_2$-laser radiation by the silane molecule. The films exhibit characteristic periodic structures along the scan direction. Figs. 4a and 4b show an optical micrograph and a Talystep analysis. The periodic structures depend neither on the scan step nor on a possible laser instability. We do not know the reason of this effect. We suppose that a permanent change of surface reflectivity and heat conductivity, in combination with the growth process, causes this phenomenon.

4. Argon ion laser-induced deposition of TiSi$_2$

First deposition runs were carried out using H$_2$ as carrier gas for the TiCl$_4$ transport into the
reaction chamber. In combination with the small spot size of about 30 μm and smaller, within the range of scan velocities of 0.02–0.2 mm/s, this carrier gas generally led to a film growth into the substrate material which was n-doped c-Si(111) in these cases, because of its absorptivity of about 63% at the argon ion laser wavelengths (VIS). The direct writing process is dominated by an etch reaction through the oxide layer into the c-Si. A film growth was observed only in the centre of the etching trench. The etching rate which was defined as the distance between the surface and the deepest point in the centre of the line depends on the TiCl₄·H₂/SiH₄ flow ratio (fig. 5a).

Films deposited in this manner show high film resistivities. The minimum value measured was 30 mΩ·cm. This poor electrical conductivity is caused by the inhomoegeneous and island-like film growth. The short illumination time of 1s ≤ 0.6 s does not allow an uniform nucleation and film growth. The EBIC micrograph (fig. 6a) shows the distribution of conducting regions and points where the passivation layer (SiOₓ) was penetrated. This electrically active zone (fig. 6a) is small compared with the total line width (fig. 6b). In order to produce uniform films the local illumination time was extended by scanning the same line two times or more in the reaction gas environment.

Fig. 7 shows a Talystep analysis perpendicular to the scan direction for TiSiₓ films on oxidized c-Si substrates. The importance of the illumination time for the nucleation and the film growth could be demonstrated by the growth of spots. At illumination times shorter than 0.5 s in the laser power range of about 0.4–1.5 W at a Gaussian radius of r₀ = 4 μm no film deposition has been observed. Fig. 8 shows the dependence of the film height on the illumination time and the pressure. Films deposited at the higher pressure of 2.6 kPa have a greater Si excess (88 at%, EDS) than films deposited at 1.3 kPa (73 at%, EDS). Increasing the illumination time for the growth of spots led to the formation of rods with lengths of some millimeters. A horizontal thickness modulation can be reached by varying the focal point in the z-direction (along the laser beam axis). Further experiments were done using the TiCl₄ vapour at the equilibrium vapour pressure (1.33 Pa). The total pressure in the reaction chamber was varied by changing the silane flow. The film resistivity could be lowered to a minimum value of 100 μΩ·cm (Pₓ = 2.6 kPa, r₀ = 0.05 mm/s, Tₓ = 300 K, P_L = 0.9 W, r₀ = 4 μm, the line was scanned four times in the gas atmosphere).

All films are silicon rich (73–90 at%). Deposited TiSiₓ lines exhibit periodic structures within the low power range (P_L < 1.7 W at r₀ = 4 μm) (fig. 9).
Fig. 9. SEM micrograph of TiSi$_{2}$ films deposited on silicon, exhibiting periodic structures ($P_{tot}$ = 10.6 kPa, $P_{L}$ = 0.85 W, $r_{G}$ = 4.5 $\mu$m, $r_{S}$ = 0.2 nm/$s$, $T_{s}$ = 900 $^\circ$K)

We do not understand the reason of their formation at this time. We believe that a periodic change in reflectivity and the related temperature-dependent deposition chemistry causes this phenomenon. Periodic structures also were observed within the high power range where melting of the surface and the growing film occurs. If the melting point is reached the reflectivity changes rapidly and less energy is deposited in the film. Therefore, the molten region solidifies and the deposition of the film material begins again.

5. Conclusions

Titanium silicide thin films have been deposited using both the CO$_{2}$-laser and the argon ion laser, corresponding to the substrates to be covered (SiO$_{2}$ or c-Si). The CO$_{2}$-laser allows the production of extended thin silicide films with deposition rates of about 60 nm/s and resistivities of 160 $\mu$\Omega \cdot$ cm. Using the argon ion laser the line width could be reduced to a minimum value of 1.7 $\mu$m. The deposition process strongly depends on the local illumination time. Film geometry, film composition and film morphology could be controlled by varying the deposition parameters gas composition, scan velocity and laser power. The laser deposition of TiSi$_{2}$ films can be developed as an alternative for the production of special devices in microsystems technology.

References