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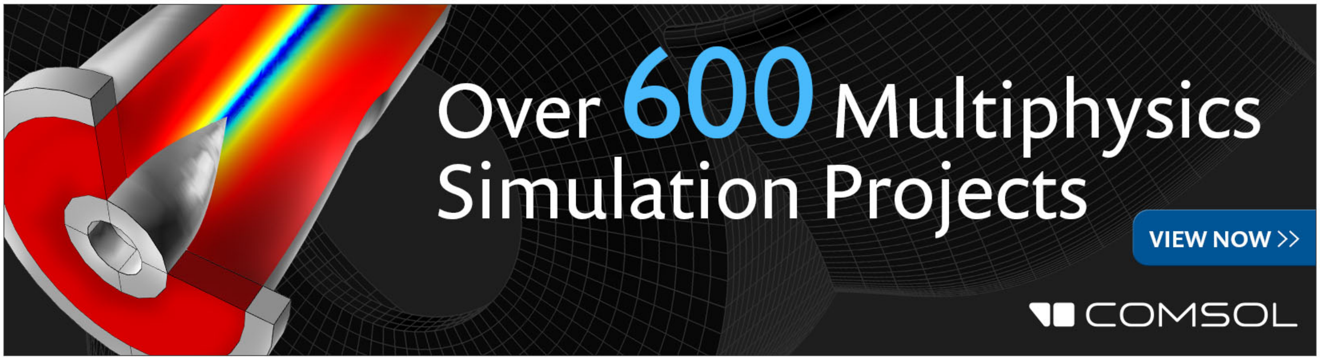

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Influence of defects on the kinetic of C49–C54 $TiSi_2$ transformation

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$TiSi_2$ C49 thin films with different concentrations of defects have been prepared by conventional annealing, in the 460–540 °C temperature range, of a Ti films deposited on a polycrystalline Si layer. The residual sheet resistance of the C49 films decreased with increasing both the annealing temperature and the annealing duration indicating the occurrence of defect annealing at higher temperature and/or longer times. A successive annealing at 650 °C was used to promote the C49–C54 transition and the transformation rate was measured by *in situ* sheet resistance measurements. The C49–C54 transition time decreased with the residual sheet resistance of the C49 phase. The activation energy for the transformation increased from 3.09 ± 0.75 to 6.12 ± 0.96 eV with increasing the defect concentration in the C49 phase. This strong dependence can explain the large variation of the kinetic results reported in the literature. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1831559]

The polymorphic C49–C54 transformation in $TiSi_2$ thin films has been largely investigated[1] during the last decade because it represents a crucial step that has to be solved in order to successfully use the titanium silicide for metallization of the submicron devices. In fact, this transformation is limited by the nucleation of the final phase, and because of the extremely low density of the nucleation sites (5×10^6 cm^{-2})[2] it becomes progressively more difficult as the dimensions of the structure shrink.

The activation energy values reported in literature are spread between 3.5 and 6 eV.[3–10] Such huge spread cannot be entirely justified on the basis of experimental errors or of the method adopted to handle the data but it could be, instead, indicative of intrinsic features of the transformation. One of the parameters that has not been controlled and that can affect the transformation rate could be the concentration of defects in the C49 phase. This phase is known to be intrinsically defective and many experimental observations[6,11] as well as theoretical calculations[12] have indicated that the C49 phase contains stacking fault. It has been suggested that the large minimum of the total energy curve versus the reaction parameters facilitates the formation of the metastable phase with respect to the C54.

In this letter we report the effect of the C49 defect concentration on the C49–C54 transition rate, in particular we will demonstrate that the C49 defect concentration affects the stability of the C49 phase and that a faster transition rate is observed when the defect density is reduced. Moreover the activation energy for the transformation vary from 3 to 6 eV as the defects in the parent phase get annealed away.

Samples were prepared by sputter deposition in an Endura system of Applied Materials. A 30-nm-thick Ti layer on a polysilicon layer (150 nm thick) was deposited on an oxidized silicon substrate. The base pressure before deposition was 10^{-9} Torr. C49 $TiSi_2$ films were formed by annealing the deposited samples in vacuum (10^{-7} Torr) at several temperatures in the 460–540 °C range for times ranging between 2 and 48 h. After the annealing the unreacted or contaminated titanium on the surface was removed by the $NH_4OH:H_2O_2:H_2O$ (1:1:5) etch at room temperature. The thickness of the silicide layer after etching was measured by Rutherford backscattering analysis using a 2.0 MeV of He and it resulted in 50 ± 2 nm on each sample. The resistance of the C49 films has been measured in the 5–320 K temperature range and the curves relatives to samples annealed at 540 °C for 2 and 48 h, and at 460 °C for 48 h are reported in Fig. 1. The resistance was constant at temperatures lower than 50 K, and had a positive slope at higher temperature as expected for a metallic layer. However, the residual sheet resistance, due primarily to the scattering of the carriers with impurities and point defects, decreased with increasing the annealing temperatures and/or the annealing time. In fact, it decreased from 12.2 $\Omega/\square$ to 9.0 $\Omega/\square$ with increasing the temperature from 460 to 540 °C for 48 h, and it decreased from 10.2 $\Omega/\square$ to 9 $\Omega/\square$ with increasing the annealing duration from 2 to 48 h at 540 °C. The residual sheet resistance could be an indication of a different defect concentration in the C49 films prepared by different thermal treatment

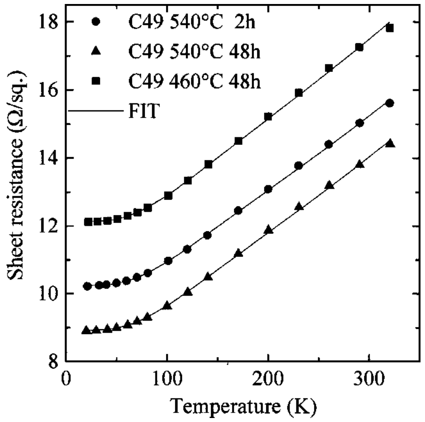

FIG. 1. Sheet resistance vs temperature for three different C49 samples annealed at different temperatures and times. The residual sheet resistance depends on both the annealing temperature and time.

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if we can rule out the presence of contaminant in the silicide. It is known that O is easily gettered by Ti atoms, so we checked the oxygen concentration in the silicide film by backscattering spectrometry using a 3.035 MeV He^+ beam. At this energy there is a resonance in the elastic scattering cross section of oxygen, and at 170° scattering angle, the cross section is about 20 times greater than the Rutherford cross section. In this configuration the minimum amount of oxygen that can be detected inside the resonance peak (12 keV full width at half maximum) is about 5×10^{15} atoms/cm^2. In order to increase our depth sensitivity we tilted the samples by 70°, and we detected in each sample a total amount of about 1.5×10^{16} oxygen/cm^2 confined within 5 nm from the sample surface, while no oxygen could be detected deeper in the silicide layer. The concentration of oxygen was independent of the thermal process to form the C49 phase so that the residual sheet resistance can be assumed to be indicative of the defect density in the film. It follows that the defect density is greater in the C49 $TiSi_2$ film formed at low temperature and for short annealing times. In order to verify that the different annealing processes do not modify the phase formed we performed x-ray diffraction measurements. The diffraction peak of the C49 (131) plane has been observed on all the samples annealed in the 460–540 °C temperature range, while no diffraction from the C54 planes could be detected.[13]

The average C49 grain size has been estimated[13] by the statistical analysis of several dark-field TEM plan-view images and it resulted 35±0.5 nm, in every sample, so that the morphology of the samples is identical within the error of TEM determination. This determination was necessary in order to rule out any effect due to a different density of triple grain boundary (which has been suggested to be the nucleation centers of the transformation) on the C49–C54 transition rate.

The transformation from the C49 to the C54 was followed by *in situ* sheet resistance at a fixed temperature of 650 °C at a pressure of 1×10^{-7} Torr. This method relies on the different resistivity of the C49 and C54 phases and has been described elsewhere.[12] The sample resistance is converted into fraction of C54 $TiSi_2$ and the transformation time is assumed to be the time at which 100% of the film has been converted into the stable phase. The transformation time was obtained from the derivative of the sheet resistance versus time curve and it is assumed to be the time difference between the points at which the derivative goes to zero. In Fig. 2 the C49–C54 transition time at the temperature of 650 °C is reported as a function of the C49 residual sheet resistance. The estimated errors on the residual sheet resistance measurements and the transition times are reported too. The C49–C54 transition time increases with the residual sheet resistance going from a minimum value of 21 min (8.86 Ω/□) to a maximum of 125 min (12.09 Ω/□). Therefore, a low defected C49 film is less stable than a highly defected film.

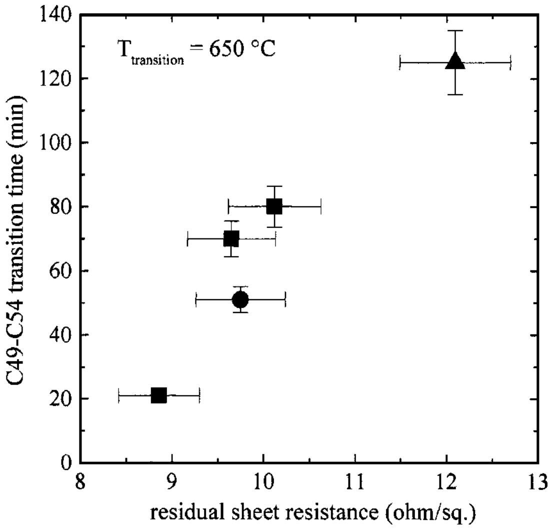

FIG. 2. C49–C54 transition time at 650 °C vs the residual sheet resistance of the C49. A correlation can be observed for different samples with the C49 formed at 460 (▲), 500 (●), and 540 °C (■).

The higher transition rate can be due to a higher nucleation rate and/or to a higher growth rate. In order to discriminate between the two possibilities we have measured the C54 grain size by collecting several Normansky optical microscopy images of the fully transformed samples. From the statistical analysis of these images the average area of the C54 grains has been measured and converted in C54 grain density. We found a maximum variation of the C54 grain size from 20.8 to 8 μm as the transformation time decreases from 125 to 21 min. The C54 average growth velocity has been estimated as the ratio between the diameter of the largest C54 grain and the time duration of the conversion annealing. This is equivalent to assuming that the largest grain nucleates at once and its size is determined only by the time available for growth. The experimental data are summarized in Fig. 3 in which the transformation time is plotted as a function of the C54 average growth velocity [Fig. 3(a)] and grain density [Fig. 3(b)]. It is evident that the reduction of the transformation time is due to the increase of either the growth velocity or grain density. The activation energy for the C49–C54 transformation depends on the defect density of the metastable phase as can be inferred from Fig. 4, where the total transformation time τ has been reported in a semilog scale as a function of $1/KT$ (where K is the Boltzmann constant). The activation energy of the C49–C54 transformation varies from 6.12±0.96 to 3.09±0.75 eV as the annealing temperature to form the C49 phase increases from 460 to 540 °C. Therefore, the activation energy of this transformation is strongly influenced by the thermal history of the

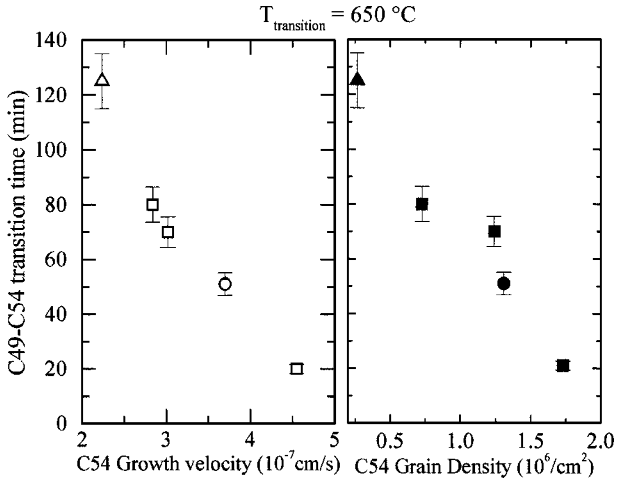

FIG. 3. C49–C54 transition time at 650 °C vs growth velocity of the C54 grains (left side) or the number of pre-existing nucleation sites per unit of area (right side). The C49 was formed at 460 (▲), 500 (●), and 540 °C (■).

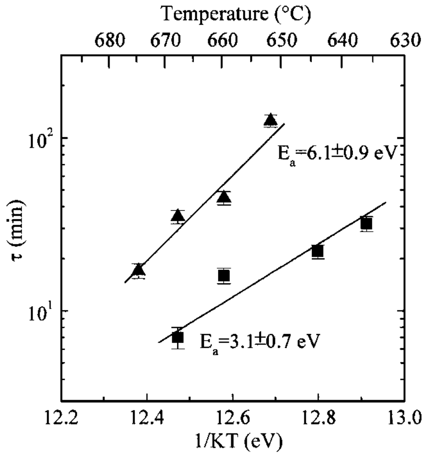

FIG. 4. Arrhenius plot of the C49–C54 transition time starting from a highly defective C49 phase, sample annealed at 460 °C (▲) or from a low defective C49 phase, sample annealed at 540 °C (■).

sample, and the huge variation observed in our samples justifies the spread of the results reported in the literature.[4–11] In a previous paper[14] it has been demonstrated that the activation energy of the C49–C54 transformation is mainly due to the growth process whilst the nucleation term is negligible. Therefore, the variation of the transformation activation energy should be related to a reduction of the barrier height for grain growth when the defect concentration in the C49 phase is lowered. Moreover, the C54 steady state nucleation rate exhibits an activated temperature dependence with an activation energy $E_n = E_G + \Delta G^*$[15,16] where E_G is the activation energy for the growth of critical nuclei and ΔG^* is the barrier height for nucleation. Although the precise value for E_G is not known, it is generally assumed to be very close to the activation energy for the grain growth. This can justify the simultaneous increase of the C54 average growth velocity and grain density with decreasing the transition time reported in Fig. 3.

In conclusion we have shown that the C49–C54 transition time depends on the thermal history of the parent phase. In particular a reduction of the transition time has been observed in samples in which the defect concentration of the C49 phase was lowered by prolonged annealing processes. The activation energy for the transformation decreases with decreasing the defect concentration and this can explain the large variation of the kinetic results reported in the literature. These effects have been interpreted in term of a reduction of the energy barrier for C54 grain growth in low defective C49 phase.

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