REACTION KINETICS OF MoSi_2 SILICIDE OBTAINED BY cw LASER ANNEALING OF Si(a) AND $\text{Si}_{\text{poly}}/\text{Mo}$ BILAYERS

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Résumé - La cinétique de croissance du siliciure de molybdène MoSi_2 a été étudiée par recuit laser en balayage de films de molybdène déposés sur du silicium amorphe ou polycristallin. Les cinétiques mesurées sont diffusionnelles dans certains cas, contrôlées par les réactions à l'interface dans d'autres cas.

Le siliciure est obtenu facilement à partir du silicium amorphe. Nous avons comparé la rapidité de formation du siliciure par réaction du métal avec le silicium amorphe ou monocristallin.

Abstract - The growth kinetics of molybdenum silicide MoSi_2 by cw scanned laser annealing of molybdenum films deposited on amorphous and polycrystalline silicon are studied. Silicide formation kinetics exhibits time dependence behaviour of interface controlled reaction in some cases and diffusion controlled reaction in others.

Silicide formation with amorphous silicon occurs quite easily. Growth rates of silicide from metal reaction with monocrystalline and amorphous silicon are compared.

I - INTRODUCTION

Refractory metal silicides are of great interest for their applications to the integrated circuit technology. In recent years molybdenum silicide MoSi_2 has been extensively investigated, the formation of this silicide generally involving a solid phase reaction between the metal layer and a single crystal silicon substrate /1,2,3/. We report here new results on the growth kinetics of molybdenum silicide by reaction of Mo with amorphous and polycrystalline silicon. Very few studies of the kinetics of Mo reaction with non monocrystalline silicon have been published so far. Moreover previous reports on the reaction between molybdenum and amorphous silicon have shown that the reaction was either inhibited or occurred at a very slow rate which was an unexpected result probably due to the presence of impurities /3,4/. To further investigate this phenomenon we have induced the reaction between metal and silicon using a scanning laser annealing technique. This technique usually allows difficulties related to impurities at the interfaces which generally hinder formation of the silicide to be overcome. Other advantages of using a scanning beam are :

- (i) Easy control of beam power ($\pm 0,1$ watt) and scan speed (± 1 %). The laser power can be chosen to complete the reaction of the whole metal layer either in a single scan or in several successive scans. This last case provides a practical mean to study the silicide growth kinetics.
- (ii) Silicide formation occurs in a short time. The annealing dwell time, typically a few milliseconds, makes possible study of growth kinetics at high temperatures (1000°C and above).
- (iii) Silicide formation can be performed in localized areas. Measurement of thickness profile across the laser annealed lines by using a standard stylus step technique (α -step) provides an adequate tool to follow the progress of the silicide front.

In our experiments, laser treatment was performed using a cw argon laser with beam diameter of $2w = 80 \mu\text{m}$ at $1/e^2$. The back surface temperature was kept constant at fixed values (25°C and 300°C). In all cases the laser scan speed used was $v = 10 \text{ cm/s}$.

Following previous works /5/ a thin overcoating layer of amorphous silicon was deposited on the molybdenum layer to provide an antireflection coating prior to laser treatment. This overcoating layer is essential to good reproductibility of quantitative results as its reflectivity remains nearly constant for all laser annealing conditions and is not dependent on the extent of silicide formation.

Information about the reaction produced was obtained by using Rutherford backscattering (R.B.S.) and X-Ray diffraction in the glancing angle arrangement. Samples for these experiments were prepared by overlapping single laser lines ($\approx 50\%$) to obtain surfaces 1 cm^2 .

II - PRINCIPE OF SILICIDE THICKNESS MEASUREMENTS

The physical phenomenon which is at the base of the difference in thickness between the reacted and non reacted regions of the sample is the volume contraction associated with the silicide formation. When the silicide is formed by reaction of the deposited metal with the silicon substrate there is a contraction in volume that can be calculated from equation :

$$\frac{\Delta V}{V} = \frac{(V_{\text{Mo}} + 2V_{\text{Si}}) - V_{\text{MoSi}_2}}{(V_{\text{Mo}} + 2V_{\text{Si}})} \quad (1)$$

where

$\frac{\Delta V}{V}$ is the relative change in volume,

V_{Mo} the atomic volume of molybdenum

V_{Si} the atomic volume of silicon

V_{MoSi_2} the molecular volume of the silicide.

For MoSi_2 either in the tetragonal or hexagonal form the volume contraction is at about 27 %. This leads, when making the alpha-step measurements to the observation of a step-down between the non reacted and the reacted regions. It is important to illustrate why this result is not in contradiction with the fact that silicon diffusion into molybdenum during the molybdenum silicide formation must provoke an increase in the metal layer volume /2/.

Fig.1 shows a photograph of a bevel of a sample which is described in detail in Fig.2.

We can notice that :

(i) The silicide regions are situated below the level of the original sample surface.

(iii) Within the limits of the annealed region an increase in volume of the layer is observed together with a step-down of the layer/substrate interface. Correlatively no long range rearrangements are observed in the silicon substrate.

(ii) From the border to the center of the annealed lines there is an observable decrease in the thickness of the molybdenum correlated with an increase in the thickness of the silicide. Due to the gaussian energy distribution of the laser spot, only at the center of the line there was enough power to form the complete silicide layer.

Fig.1 Bevel of a Si/Mo/Si structure. The angle α of the bevel is equal to 15° .

Fig.2 Schema of the bevel observed on Fig.1.

The α -step profiles are shown in Figure 3. The same effects already shown in the previous figures are observed that is the step-down between annealed and non annealed regions and the gaussian profiles.

Fig.3 α step measurement for repetitive laser scans. The whole metal layer has reacted after four scans.

Moreover the α -step technique can give quantitative results illustrated in the following numerical example. For a 100 Å of molybdenum layer, 254 Å of silicon react to form 259 Å of molybdenum silicide as calculated from equation(1). The difference between the thickness of the molybdenum plus silicon involved in the reaction and the thickness of the silicide will be measured by the α -step. The measured values represent 0,95 of the reacted molybdenum thickness at each stage in the silicide formation. Evolution of silicide thickness for different laser powers or for several laser scans over the same line at constant power can be easily measured using this technique. Accuracy of measurements can be estimated at better than 50 Å . To check the validity of this technique we have performed classical R.B.S. analysis. Within the limitations in depth resolution of the R.B.S. technique a good agreement is found with alpha-step measurements.

III - RESULTS

In order to study the silicide formation we have prepared different test samples listed in table I.

E ₁	Si mono / SiO ₂ / Si(a) / Mo / Si(a)
E ₂	Si mono / SiO ₂ / Si poly / Mo / Si(a)
E ₃	Si mono / Si(a) / Mo / Si(a)
E ₄	Si mono / Si poly / Mo / Si(a)

The inner silicon films were obtained by LPCVD deposition on Si/SiO₂ or Si<100> substrates. The deposition temperature was 525°C for amorphous silicon and 625°C for polycrystalline silicon, the other conditions being identical.

After removal from the LPCVD furnace, the samples were etched in dilute HF, nitrogen dried and placed in a doublegun electron evaporator system where Mo/Si(a) layers were sequentially deposited without breaking the vacuum. Vacuum conditions were $\approx 10^{-7}$ torr background pressure and $1-6 \cdot 10^{-6}$ torr during evaporation with deposition rates being Mo $3-10 \text{ \AA/s}$ and Si $\approx 1-3 \text{ \AA/s}$. For all the samples silicide formation was obtained in a single scan if an appropriate laser power was used. We never found reaction between the outer amorphous silicon layer and the molybdenum layer in any of the experiments. This is a phenomenon that has been previously observed and discussed /6/. In all cases the silicide formed presented the hexagonal structure of MoSi₂. This is another curious result since the effective temperature during laser annealing is always higher than 700°C which is generally considered as the transition temperature between the hexagonal form of MoSi₂ and its tetragonal form expected at high temperature /7/. Recently the same result has been found for pulsed electron annealing of Mo/Si structures at temperatures higher than 1400°C /8/. Experiments are in progress to further investigate this phenomenon.

For samples (E₁, E₃), silicide formation can be detected for relative powers $P/P_0 > 0,65$, where P is the laser power and P₀ the laser power (determined experimentally) required to melt the silicon substrate at the scan speed used. No amorphous-polycrystalline silicon transformation has been observed at the relative laser-powers used to study the silicide growth kinetics.

For samples (E₂, E₄) silicide formation can be measured from relative powers $P/P_0 > 0,75$.

For both samples at P/P_0 lower than these thresholds the silicide formation still occurs but it can be detected only after several successive scans over the lines. We can first conclude from these rather small relative laser powers that the reaction of Mo with amorphous or polycrystalline silicon is easy to induce. These results also indicate greater interaction of molybdenum with amorphous silicon than with polycrystalline silicon.

On Fig.4 is plotted, for sample E₁, the square of the silicide thickness versus the number of repetitive laser scans. The data points shown have been calculated from the α -step measurements. Since the number of laser scans represents an effective annealing time the results give the kinetics of silicide formation. It is clear from the figure that silicide growth follows a parabolic law as a function of the number of repetitive scans. This behaviour is found for reactions controlled by diffusion and leads to the following expression :

$$Z^2 = R_0 t_{\text{eff}} \exp \left(\frac{-E_a}{T_{\text{eff}}} \right) \quad (2)$$

where Z is the silicide thickness, R₀ a pre exponential constant, t_{eff} the effective annealing time and T_{eff} the effective annealing temperature.

Fig.4 Sample E1 : Square of MoSi₂ thickness as function of the number of laser scans.

However to the best of our knowledge there are no appropriate models, owing to the existence of a thick SiO₂ film, to calculate T_{eff} values as a function of the laser power and no attempt to calculate an activation energy has been made so far [9]. For the other samples E₂, E₃, E₄ the kinetics of silicide formation was controlled by reaction at the interface. This shows that even in the case of laser annealing, impurities (mainly oxygen and carbon [6]), in the layers or at the interface lead to the same problems found in furnace annealing for which large discrepancies exist in the literature as to the kinetics of the formation of MoSi₂ [1,2]. Unfortunately, unless samples are prepared in U.H.V., the presence of impurities cannot be avoided and only exact knowledge of the pressure and composition of the residual atmosphere and of evaporation rates could ensure sample reproducibility. This is an important point for people working in the technological field. Systematic studies to improve our deposition methods are being undertaken.

Fig.5 Sample E₂ : MoSi₂ thickness as function of number of laser scans.

Fig.6 Sample E₃ : MoSi₂ thickness versus the number of laser scans. The value of P_0 is 6.2 w.

Fig.7 Sample E₄ : Silicide thickness versus the number of laser scans.

Fig.8 MoSi₂ thickness obtained for a single laser scan versus the effective annealing temperature.

Silicide thicknesses measured for E₂ are reported on figure 5. A law of general form,

$$Z = \left\{ R_0 t_{\text{eff}} \exp \left(- \frac{E_a}{kT_{\text{eff}}} \right) \right\}^n \quad (3)$$

is inadequate to describe these data. After the beginning of a reaction a very slow silicide front advance is observed. The silicide thicknesses measured on E₃ as a function of the number of laser scans are plotted in Fig.6. The kinetics found correspond to an interface controlled reaction following the equation :

$$Z = R_0 t_{\text{eff}} \exp \left(- \frac{E_a}{kT_{\text{eff}}} \right)$$

For this structure the analytical model given by Gold and Gibbons /10/ can be used to calculate values for T_{eff} and t_{eff} depending on experimental conditions, and to deduce the activation energy E_a of the reaction. E_a is given by the slope of the curve $\ln(Z/n)$ (where n is the number of laser scans) versus $1/T_{\text{eff}}$. The value for E_a thus found is $E_a = 2,5 \pm 0,2$ eV. Sample E₄ is representative of most of the problems arising from the presence of impurities. It is clear from Fig.7 that silicide formation only starts after a number of laser scans which increases for decreasing laser powers. When a reaction starts, the silicide growth follows a linear law. In this case, activation energy can be calculated but comparison of activation energies for reactions which follow different kinetics mechanisms would be meaningless. One can still make, however, qualitative comparisons of the reaction rates. This is shown in Fig.8 where the silicide thicknesses reached for a single laser scan are plotted as a function of the effective annealing temperature T_{eff} . Previous results for silicide formation by laser annealing of metal layers on single crystal silicon are plotted as well. The measured reaction rates for amorphous and polycrystalline silicon are probably below the values that we should have observed in case of a diffusion mechanism. The interfacial reaction generally is the slowest process and parabolic growth can only be observed when the interfacial reaction is fast enough /11/.

IV - CONCLUSION

We have shown that the reaction of amorphous and polycrystalline silicon with molybdenum metal layer to form MoSi₂ silicide is easily obtained using laser annealing. The intrinsic mechanism in the absence of impurities is controlled by diffusion. However even at the high temperatures of laser annealing treatments the presence of impurities in the layers or at the interfaces are responsible for different kinetics behaviours as it is generally found during standard furnace annealing. We have also reported the use of a simple and accurate experimental technique to measure the silicide growth based on the volume contraction associated with the silicide formation.

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