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A conductance model (approach) for kinetic studies: The Ti–Ta–Si system

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Electrical resistance measurements provide a convenient way to study the kinetics of transformations in isothermally annealed thin films. The measured resistance and the amount of a new phase formed during some sort of reaction in a transformation process are often related by a linear function. This simple relationship between the measured resistance and the fraction of the new phase formed is not always valid and the reliability of the results might be questionable. In this communication, a different approach is suggested, which is based on conductance. The validity of the model is tested by experimental data for the Ti–Ta–Si system. The suggested and the linear resistance models are compared, and it seems that it is more appropriate in certain cases to use the conductance approach for kinetic purposes. An effective activation energy can be derived from the results by defining the time needed at each temperature to obtain either a constant resistance, or alternatively, a certain fraction of the new phase. The activation energy derived for the end phase, i.e., (Ti,Ta)Si\(_3\) formation from the experimental data in the example (Ti–Ta–Si) considered is \(\sim 2.6\) eV. © 2000 American Vacuum Society. [S0734-2101(00)04706-0]

I. INTRODUCTION

One of the common methods to follow the progress of phase transformation or a reaction between reacting components in a system is to measure the change in resistance that accompanies the process. Often a linear dependence between the resistivity and the volume fraction of an isothermally transformed material is assumed in order to relate the change in the resistivity to the progress of the transition. Such a transformation or a reaction between reacting components in a system is to measure the change in resistance that accompanies the process. Often a linear dependence between the resistivity and the volume fraction of an isothermally transformed material is assumed in order to relate the change in the resistivity to the progress of the transition. Such a relation was widely used in various phase transformations as indicated in the literature.\(^1\)–\(^5\) However, in many cases this model is not valid. Even the evaluation of the formation of a new phase in a homogeneous environment of an old phase by the linear approximation of the resistivity change might sometimes be a complex problem. More so, the use of the accepted linear approximation to calculate the formation of a new phase in the simultaneous presence of intermediate phases might be oversimplified, and the reliability of the results might be questionable.

In this communication, we suggest a different approach for the use of the experimentally measured resistivity data for kinetic purposes in those cases where the parent phase is not homogeneous or when nucleation and growth (or phase transition) is accompanied with the formation of an intermediate phase before the final and stable phase is obtained. A conductance model is the basis of our proposal. The approach to be described is in particular expected to be appropriate, when the intermediate phase (or one of the phases) has a high resistivity as compared with the stable end phase. This is the case in many silicides. For example, a high resistivity metastable disilicide (80–100 \(\mu\)Ω cm) always appears first\(^1\) as an intermediate phase before the stable phase (\(\sim 15\) \(\mu\)Ω cm)\(^2\) forms in the Ti–Si system. Similarly, in the case of the Ta–Si system, the high resistivity Ta\(_3\)Si\(_3\) might form before the stable TaSi\(_3\) phase. In this article, the nonlinear resistivity model will be discussed in Sec. II. Testing the model will be done with experimental data obtained in the Ti–Ta–Si system. This will be followed in Secs. III and IV by the experimental details and results of the Ti–Ta–S system. Finally, Sec. V is the conclusion.

II. COMPARISON BETWEEN THE CONDUCTANCE AND RESISTANCE MODELS

The resistance model assuming a linear dependence between the value of \(R\) and the fraction \(X\) of a phase formed\(^1\)–\(^6\) is expressed as

\[
X = [R_0 - R]/[R_0 - R_f],
\]

where \(R\) is the measured resistivity as a function of time, \(R_0\) and \(R_f\) represent the initial resistances of the as deposited film and the final phase, respectively. Equation (1) can be rewritten as

\[
R = XR_f + (1 - X)R_0.
\]

This formula corresponds to the case when the resistances of the two phases \(XR_f\) and \((1 - X)R_0\) are connected in series and it is most appropriate when the measurements of the film resistance are made from the two sides of the film. Regardless, if the additional phase forms layerwise or it is dispersed in the film, when the resistance is measured between surface points (like in a four probe measurement) a better assumption would be if the film conductance \(C\), would be evaluated by a parallel connection, i.e., by the addition of the conductances \(XC_f\) and \((1 - X)C_0\). Here obviously, \(C_f\) final and \(C_0\) initial represent the conductance of the film. The expression is given below in terms of resistances as

\[
\frac{1}{R} = \frac{X}{R_f} + \frac{1 - X}{R_0}.
\]
Moreover, physical support for such an approach in the case when one of the phases in a thin film has a high resistivity, whereas the other has a substantially lower resistivity is obvious. Under such conditions, the high conductivity phase predominantly carries the current with a negligible contribution from the high resistivity phase or phases and the conduction current path is through the low resistivity component. Figure 1 expresses the relation between $X$ and $R$ according to Eqs. (2) and (3). The experimental points were obtained from resistivity measurements in the Ti–Ta–Si system, and the fraction $X$ of $(\text{Ti,Ta})\text{Si}_2$ formed by isothermal annealing was evaluated from x-ray diffraction (XRD) intensity data. The ratio of the sum of intensities of the various $(\text{Ti,Ta})\text{Si}_2$ reflections at each time of the isothermal annealing to the sum of the intensities of the final end phase in the film, corresponding to $(\text{Ti,Ta})\text{Si}_2$ are the points plotted in Fig. 1 versus the respective film resistivities. It is obvious that the approach suggested in this communication, i.e., Eq. (3), describes far better the $X$ versus $R$ relation in the Ti–Ta–Si system than the commonly used Eq. (1). It is our belief, that in other systems also, where a very low resistivity constituent together with a high resistivity phase coexist for some time in the film, Eq. (3) might be a better approach to derive values of the fraction of some phase formed in the progress of its formation in a phase transformation process.

It should be noted that Eq. (3) leads to the linear resistance dependence, Eq. (2), in the limiting case when $R_{\text{eq}}$ is reasonably close to $R_f$. This is shown in the Appendix.

The next sections describe the experimental details of $(\text{Ti,Ta})\text{Si}_2$ formation.

### III. EXPERIMENT

Experimental details of $(\text{Ta,Ti})\text{Si}_2$ formation in thin films were discussed in a recent publication and the thermal conditions for its formation were indicated. Briefly, Ti and Ta were codeposited to a thickness of 200 nm at rates of 0.08 and 0.1 nm s$^{-1}$, respectively, on $n$ type Si(111) substrates. After accepted cleaning methods, the Si wafers were loaded into an electron gun evaporation chamber which was equipped with two guns for codeposition. The initial vacuum level in the chamber was $1.13\times10^{-4}$ Pa. The rates applied would have resulted in 110.5 and 89.2 nm individual layers of Ta and Ti, respectively, if in a bilayer configuration. The film exhibited a poorly crystallized structure which showed peaks of Si, and Ti and Ta centered at $2\theta=28.5^\circ$ and $2\theta =38.5^\circ$, respectively, and a humplike Ta and Ti region at about $2\theta=69.6$. Specimens sliced from these wafers were subsequently exposed to rapid thermal annealing (RTA) in a nitrogen atmosphere in the temperature range of 1023–1223 K for up to 300 s. The structure of the as-deposited and annealed specimens were analyzed by XRD measurements with Cu$K_a$ radiation at each stage of the processing on the same specimens that were used for resistivity measurements.

Sheet resistance measurements were performed as a routine, using a four-point probe before annealing and at all stages of annealing to see the progress of silicidation.

### IV. RESULTS AND DISCUSSION

Figures 2–4 summarize the XRD results obtained after isothermal RTA at the temperatures indicated. The progress of $(\text{Ti,Ta})\text{Si}_2$ formation at 1023 K is slow and the presence of intermediate phases was observed. At 1123 K, the progress of $(\text{Ti,Ta})\text{Si}_2$ formation was fast and the film consisted almost entirely of this phase after 200 s annealing. The film was composed almost completely of $(\text{Ti,Ta})\text{Si}_2$ at 1223 K already after 5 s RTA.

The results of the resistivity measurements are consistent with the diffraction results and they confirm the progress of the reactions inferred from the XRD data. The unreacted samples of the as-deposited films on Si (111) exhibited a sheet resistance of $\sim 13.7 \Omega/\square$. These correspond to $\sim 27.3 \mu\Omega \cdot \text{cm}$. The variation of the sheet resistance as a function of RTA time is summarized in Fig. 5 and the graphs are in conformity with the results of the XRD data. The as-deposited films, which are poorly crystallized or amorphous as identified by x-ray diffraction, had high sheet resistance. The film resistance continuously decreased with RTA annealing time and it can be related to the progress of crystallization and the specific transformations taking place. The drop in the film resistance with annealing time is due to the increase in volume fraction of the low resistivity reaction products and is in accordance with the XRD results. The sheet resistance of the completely reacted film on Si (111) at 1223 K, resulting in $(\text{Ti,Ta})\text{Si}_2$ solid solution, was $2.23 \Omega/\square$ and it remains at about this low saturation value with further annealing. At this temperature the interaction—leading to the formation of $(\text{Ti,Ta})\text{Si}_2$ with the lowest sheet resistance—takes place almost instantaneously. The resistance value obtained is between those of C54 TiSi$_2$ and TaSi$_2$. The formation of $(\text{Ti,Ta})\text{Si}_2$ at 1123 K on Si(111) is very fast but is not completed within the time interval of the experiment, and an additional RTA of $\sim 100$ s would be sufficient to achieve completion. At a temperature of 1023 K, the high sheet re-
sistance is a result of the presence of high resistivity phases of Ta and/or Ti rich silicides and their contribution to the overall value.

In Fig. 1, the experimental results were added to the calculated curves according to Eqs. (2) and (3). The intensity values were measured on the same specimens that were used for the XRD. The values of $X$ were calculated from the sum of the XRD intensities corresponding to the $(hkl)$ reflections from the $(Ti,Ta)Si_2$ phase, and they were related to the sum of reflections of a specimen where the film consisted only of this phase. The accuracy of the $X$ values are obviously subject to the accuracy of the intensity data. In the light of the fact that the original objective of the experiments was not exact intensity evaluation, the spread in the curves can be considered as reasonable and proving the use of Eq. (3) for kinetic studies.

In order to relate the change in resistance to the progress of a phase formation (in our case that of $(Ti,Ta)Si_2$) Eq. (3) can be used to define the volume fraction. The values of $R_f$ and $R_0$ and $R$ are measured. The temperature dependence of the rate of this phase formation can be obtained by defining a time constant, $\tau$, at which some fraction of the phase under consideration is obtained. Usually, $X(\tau) = 1/2$ is chosen for this relation according to

$$\ln(\tau_{0.5}) = \frac{E_{\text{app}}}{RT} + \text{constant.}$$

An apparent activation energy, $E_{\text{app}}$, for the formation of $(Ti,Ta)Si_2$ can be obtained by plotting the time needed to obtain the half volume fraction of this phase against $1/kT$. From Fig. 1, a value of $\sim 4.4\Omega/\square$ corresponds $X_T = 1/2$. Knowing this value of the sheet resistance, the time needed to obtain such a fraction at each temperature can be obtained from Fig. 5.

Alternatively, the variation of sheet resistance of the cosputtered film with time was used by Murarka and Fraser to study the kinetics of TiSi$_2$ formation. In line with their approach, if it is assumed that a given value of sheet resistance of a film is the sum of the contributions from various chemical and structural components and it essentially represents a certain film composition, the temperature dependence of the reaction taking place can be obtained by plotting time to obtain a given value of sheet resistance as a function of temperature. Figure 6 is such a plot. Conveniently the time to obtain a sheet resistance of $4\ \Omega/\square$ was chosen (also used in

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Fig. 2. XRD spectra of a Ti–Ta film, deposited on Si (111) and RTA at 1023 K for the times indicated.
In the (Ti,Ta)Si$_2$ formation case, this sheet resistance is apparently close also to the $1/2$ fraction ($\approx 0.57$). According to the data of Fig. 5, the lowest sheet resistance at 1223 K after 5 s RTA was 3.7 $\Omega/\square$ representing according to the x-ray results (Fig. 4) almost entirely (Ti,Ta)Si$_2$. At 1123 K the time to reach 4 $\Omega/\square$ is $\approx 100$ s and the time to obtain it was interpolated between the respective experimental data. The time value to obtain 4 $\Omega/\square$ at 1023 K was obtained by extrapolating the 1023 K line of Fig. 5. Two regions can be seen in Fig. 5, in particular at 1023 K, which might suggest that two mechanisms operate. At the high temperatures, one mechanism, i.e., the vanishing of the metal rich phase, is very fast, but at 1023 K it is relatively slow. The almost linear portion in the second region of the lines is assumed to represent the formation of (Ti,Ta)Si$_2$. The time values corresponding to a sheet resistance of 4 $\Omega/\square$ show an Arrhenius type plot as a function of the inverse temperature (Fig. 6). A linear fit (correlation factor of the fitting is 0.997) through the points yields an effective activation energy of $\approx 2.6$ eV for the overall reaction for (Ti,Ta)Si$_2$ formation on Si (111).

The reliability of this value might be questionable, since only three data points were available and it would be desirable to have additional data points. However, low temperature annealing would not be of great help, since at lower temperatures no complete solid solution formation occurred$^{9-11}$ whereas at higher temperatures than 1223 K, the rate of (Ti,Ta)Si$_2$ formation is very fast. This kind of estimation could not be made for (Ti,Ta)Si$_2$ films on Si (110), since no sufficient data were available. Recalling that (Ti,Ta)Si$_2$ is isomorphous with TaSi$_2$ it would be expected to obtain an activation energy close to that obtained for TaSi$_2$. An activation energy of 3.7 eV was reported in the literature for TaSi$_2$ formation$^{12}$ but also a value of 2.5 eV is quoted in the same reference, which is more in keeping with the results of other investigations on the formation of transition metal disilicides. In another isomorphous compound, namely WSi$_2$, activation energies of 2.7–3.1 eV$^{13}$ and 3.0 eV$^{14}$ were given, which are in line with the activation energy value of 2.6 eV for the growth of (Ti,Ta)Si$_2$. The growth law of TiSi$_2$ depends on substrate orientation,$^{15}$ and a value of 2.5–2.6 eV was determined for the activation energy. Lower values for the growth of TiSi$_2$ were also reported by various
techniques, and the variation in the results were analyzed in Ref. 14 in favor of the value of 2.5–2.6 eV. The reproducibility of results reflected in the wide variation of the values of the activation energy reported in the literature (for almost all disilicides not only for TiSi₂) depends on the experimental conditions. The above quoted activation energy values were adopted for comparison with the results of this work. Thus, it is seen, that the value of the effective activa-

**Fig. 4.** XRD spectra of a Ti–Ta film RTA on Si (111) at 1223 K for the times indicated.

**Fig. 5.** Sheet resistance of films as a function of RTA time at the temperatures indicated.

**Fig. 6.** Arrhenius plot of time to obtain 4 Ω/□ vs 1/T. Activation energy is 2.6 eV.
tion energy of \( \sim 2.6 \) eV for (Ti,Ta)Si2 formation obtained in this preliminary study is in line with results of other investigations on the formation of transition metal disilicides reported in the literature. It would be desirable that additional investigations should be undertaken to confirm the results of this study.

V. CONCLUSIONS

A conductance model has been suggested to study the kinetics of phase formation in thin films. The relationship between resistance and the amount of the phase formed has been evaluated by this model for the case of (Ti,Ta)Si2. Good agreement exists between the experimental data and the line calculated according to the conductance model. An apparent activation energy of \( \sim 2.6 \) eV for this phase formation was derived from the slope of an Arrhenius plot. It is thus recommended that if resistivity data are used for kinetic studies, preliminary testing should be performed to establish which of the models, the conductance or the resistance approach, describe more appropriately the reactions taking place in a particular system.

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APPENDIX A: LINEAR RESISTANCE DEPENDENCE AS THE LIMITING CASE

If \( R_f = R_0(1 - r) \) where \( r = (R_0 - R_f)/R_0 \) is small then Eq. (3) can be rewritten as

\[
R = \left( \frac{X}{R_f} + \frac{1 - X}{R_0} \right)^{-1}, \tag{A1}
\]

and in terms of \( r \)

\[
R = R_0 \left( \frac{X}{1 - r} + 1 - X \right)^{-1}. \tag{A2}
\]

Substituting for \( r \) in Eq. (3) as indicated in the following equation

\[
\delta = \frac{R_{RM} - R_{CM}}{R_{RM}}. \tag{A5}
\]

RM and CM in Eq. (A5) refer to the resistance and conductance models, respectively. One can plot the relative deviation versus the fraction transformed for various values of \( r \) by Eqs. (2) and (A1) as seen in Fig. 7. The value of \( r = 0.81 \) in the plot was chosen on the basis of the experimental data. As can be seen the deviation decreases with \( r \). Indeed according to Eqs. (A4) and (A5) the deviation approaches zero for small \( r \) as indicated in the following equation

\[
\delta = \frac{r^2 X(1 - X)}{1 + r X}. \tag{A6}
\]