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Ellipsometry as a tool for studying an intermetallic growth

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Abstract. The sensitivity and usefulness of the ellipsometric measurements for studying the intermetallic growth processes and the application of an appropriate algorithm for extracting the information from experimental data is demonstrated. Our new numerical algorithm for depth profiling of inhomogeneous layers is applied to the experimental ellipsometric data of S-H Ko *et al* (published in *Journal of Applied Physics* in 1992) obtained for the formation of $CoSi_2$ from CoSi during rapid thermal annealing at 650 °C. Derived depth profiles of $CoSi_2$ volume fraction in the cobalt silicide layer for different annealing times are interpreted as the result of an Si diffusion along growing $CoSi_2$ grain boundaries. Then the grain boundary diffusion coefficient of Si is determined by fitting experimentally obtained Si diffusion profiles with analytical functions predicted by the theory of diffusion in thin films.

1. Introduction

In recent times intermetallic films—silicides of metals such as nickel, cobalt, palladium and titanium—have received considerable attention for their use as ohmic contact materials in very-large-scale integrated circuits [1].

Much work is devoted to understanding the basic mechanisms of the silicide formation and the associated reaction kinetics. The studies usually involve surface-sensitive methods such as x-ray diffraction, XPS, RBS, SIMS, AES, REEM, cross-sectional TEM, and high-resolution TEM.

Because of the large extinction coefficient of metals and metallic alloys ellipsometry as a tool for investigations has the restriction of a low optical penetration depth. However, for extremely thin films (<100 nm) the effect of large extinction coefficient can be eliminated. It has been demonstrated [2–4] that ellipsometry is sensitive to phase transformation during the silicide growth and it could be successfully used to give some insight into the reaction mechanisms.

Ko and coworkers [4] have investigated the formation of cobalt disilicide, $CoSi_2$, induced by rapid thermal annealing (RTA) of very thin CoSi on Si by ellipsometry. In their paper the calculations of the inverse problem of ellipsometry are based on the two-layer model for the silicide with two adjustable parameters: the thickness of the growing $CoSi_2$ layer and the refractive index of the top layer. It is found that the refractive index of the top layer decreases with the time of annealing.

In our recent paper [5] we developed a new numerical algorithm for ellipsometric data interpretation that provides reliable information on the compositional profiles with depth in composite inhomogeneous layers and interfaces. The variation of the volume fraction of the constituents with depth is obtained by the Bruggeman effective medium theory [6] without the multilayer model parametrization.

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In this paper, using the ellipsometric data given in [4] we extract further detailed information about the kinetics of the growing process of the disilicide layer by our numerical algorithm for ellipsometric data interpretation.

2. The numerical analysis of ellipsometric data

2.1. Details of the numerical algorithm for evaluating depth profiles from ellipsometric data

Let consider an optical model where an inhomogeneous layer of thickness d, whose optical constants are of interest, is embedded in a given stratified medium.

The direct problem of ellipsometry for this structure could be represented symbolically by a nonlinear operator equation:

$$\rho(\theta, k) = Af(x) \tag{1}$$

where ρ is the ratio of the complex reflection coefficients for p- and s-polarized light with a wavenumber k, incident at angle θ on the surface. Here A is a nonlinear operator that represents all the mathematical operations for calculating ρ from a given depth profile $f(x)$. The function $f(x)$ could denote the dielectric constant, volume fraction of the constituents of a heterogeneous layer, chemical composition, etc.

In our recent papers [5, 7, 8] the Newton–Kantorovitch method for solving nonlinear operator equations is used to construct numerical algorithms for the ellipsometric depth profiling. They work directly with functions and operators under a general assumption that the unknown profile is a smooth function with depth.

Similar algorithms could be derived also using the Newton–Gauss method [9] for solving nonlinear operator equations. Here a brief representation of such an algorithm will be given.

According to the Tikhonov regularization method [9] for solving ill posed problems, the problem of the solution of equation (1) is replaced by the problem of minimization of the functional

$$M(f) = \|Af - \rho^*\|^2 + \alpha\|Rf\|^2 \tag{2}$$

with respect to the unknown function $f(x)$. Here R is the regularizing operator and $\alpha > 0$ is the regularization parameter. The regularization operator carries out the *a priori* assumed smoothness of the unknown function $f(x)$. In our calculations we use a regularizing operator

$$\|Rf\|^2 = \int_0^d |f(x)|^2\,dx + \int_0^d |df(x)/dx|^2\,dx.$$

The main component of the functional (2) is the squared norm of the difference between known (experimentally measured) values ρ^* of the ellipsometric ratio and calculated values of ρ from a given estimate to the unknown profile $f(x)$. It is analogous to the sum of squares that is subjected to minimization in the statistical estimation of discrete parameters from experimental measurements.

If the Frechet derivative of the operator A is known then this operator could be linearized. The linearization of the operator A in the functional of the squared norm of the difference between the values measured and calculated from the model is known in the literature as the Newton–Gauss procedure [9].

Let $A'(f_n)$ be the Frechet derivative and $A'(f_n)(f - f_n)$ the Frechet differential of the operator A for a given estimate f_n of the unknown function f. Then A could be linearized in the neighbourhood of f_n as follows:

$$A(f) = A(f_n) + A'(f_n)(f - f_n) + O(\|f - f_n\|). \tag{3}$$

Making the following definitions:

$$B \equiv A'(f_n)$$

and

$$v \equiv \rho^* - A(f_n) + A'(f_n) f_n$$

we could rewrite the operator (2) in the form

$$M(f) = \|Bf - v\|^2 + \alpha \|Rf\|^2. \tag{4}$$

Then a better estimate f_{n+1} could be obtained by minimizing the functional (4) with respect to the unknown function f.

Thus, the Gauss–Newton algorithm for solving the inverse problem of ellipsometry is an implementation of the following iterative procedure: starting from an initial guess of the unknown profile and calculating each subsequent estimate to the solution, by minimizing the functional (4). The final result is a profile that fits experimental data.

The upper limit of the error variance in the calculated profile, resulting from measurement errors in the ellipsometric data, could be estimated from the residual of the minimization [10].

The Frechet differential of the operator A is given in our earlier works for the function $f(x)$ representing a complex dielectric profile [7], a damage depth profile [5] and compositional profile [8].

The numerical method used for the minimization of the functional (4) is not of principal importance. It could be any method suitable for minimization of quadratic functionals. The conjugated gradients method is used in our computer programs.

2.2. The determination of compositional profiles of the cobalt silicide layer

$CoSi_2$ is an interesting candidate to use in the modern semiconductor industry since is has one of the lowest resistivities among all silicides.

The reaction between a layer of Co and Si has been extensively investigated [4, 11–17]. Upon heating initially, Co_2Si and CoSi form simultaneously and, when all of the Co has been consumed, Co_2Si is converted into CoSi. Finally, at temperatures above 500 °C, CoSi is transformed into $CoSi_2$ by a further reaction with the Si substrate. On monocrystalline Si, the transition from CoSi to $CoSi_2$ occurs by a complex mechanism and growth kinetics.

In the paper of Ko *et al* [4] CoSi is formed from 22 nm Co film sputtered onto Si substrates and annealed in a rapid thermal annealer at 575 °C for 90 s. Its thickness has been evaluated about 42 nm. Then CoSi samples are annealed at 650 °C for several annealing times. After each anneal multiple-angle-of-incidence (21 equidistant angles between 60° and 80°) ellipsometric measurements are performed at 632.8 nm. The ellipsometric responses of the samples have been simulated using a model for the two layers (a layer of CoSi and a layer of $CoSi_2$) on an Si substrate. Such a model cannot solely explain the evolution of

ellipsometric data with time. A better fit was obtained when a real part of the top CoSi layer was allowed to vary in time. This result could be attributed to a rough CoSi/$CoSi_2$ interface or, in our opinion, to inhomogeneity of the top layer due to an intermixing process during growth of $CoSi_2$ in the RTA regimes.

It could be supposed that the silicide layer consists of two phases of cobalt silicide ($CoSi_2$ and CoSi) with varying volume fraction in depth and in time. Under such an assumption, we tried to obtain more information from the ellipsometric data, applying our algorithm for evaluation of compositional depth profiles.

The Bruggeman effective medium theory [6] is used to calculate the optical constants of the silicide layer that have been modelled as a mixture of $CoSi_2$ and CoSi with refractive indices 2.2−i1.34 and 3.2−i2.44 respectively [4]. The Bruggeman effective medium theory assumes an aggregate structure of the layer, being a random mixture of the two phases.

The optical model of a homogeneous silicon substrate with an inhomogeneous top layer has been assumed. The calculations are performed for different thicknesses of the layer, fixed during the minimization. We accept the thickness and the compositional profile as a successful solution if the residual from minimization is minimal and the volume fraction of the $CoSi_2$ reaches a value of unity near the substrate (corresponding to the continuous $CoSi_2$ region formed on the silicon).

Calculated profiles of $CoSi_2$ volume fraction against depth are shown in figure 1 (*a–e*) for annealing time 10 s, 20 s, 30 s, 60 s and 75 s respectively. The estimated mean error in the volume fraction is ~0.04. Obtained thicknesses are 40 nm, 55 nm, 62 nm, 70 nm and 71.5 nm respectively. A variation of ±1 nm in the thicknesses leads to a difference in profiles within estimated error bounds.

Two distinguished regions are seen in the depth profiles:

(A) A region of $CoSi_2$ formed on the silicon substrate with a thickness increasing with the time of annealing.

(B) A surface inhomogeneous region with the presence of two phases ($CoSi_2$ and CoSi) of the cobalt silicide. Their ratio changes continuously with depth.

The thickness of the $CoSi_2$ region (A) versus the square root of the treatment time is plotted in figure 2. The data fit as a straight line, the extrapolation of which gives a value of 10 s for the time at which the continuous $CoSi_2$ layer is initially formed.

3. Discussion

There are two possible mechanisms of formation of $CoSi_2$ from CoSi:

(i) $2CoSi \rightarrow CoSi_2 + Co$ followed by a Co diffusion through already formed disilicide to the silicon substrate where the reaction $2Si + Co \rightarrow CoSi_2$ takes place;

(ii) $CoSi + Si \rightarrow CoSi_2$, where a Si diffusion in the CoSi layer from the silicon substrate is required.

There is no general agreement in the literature as to what is the dominant process in the disilicide grain growth during annealing.

It is known [18] that the grain boundary diffusion of species plays an important role in the reactions in thin films. A mathematical analysis of the diffusion processes in the polycrystalline films with parallel vertical grain boundaries [19] gives analytical expressions for the concentration profiles of the diffused component, that include the diffusion coefficient D_l for the diffusion in the crystalline material and the grain boundary diffusion coefficient D_b. These concentration profiles have a complicated structure.

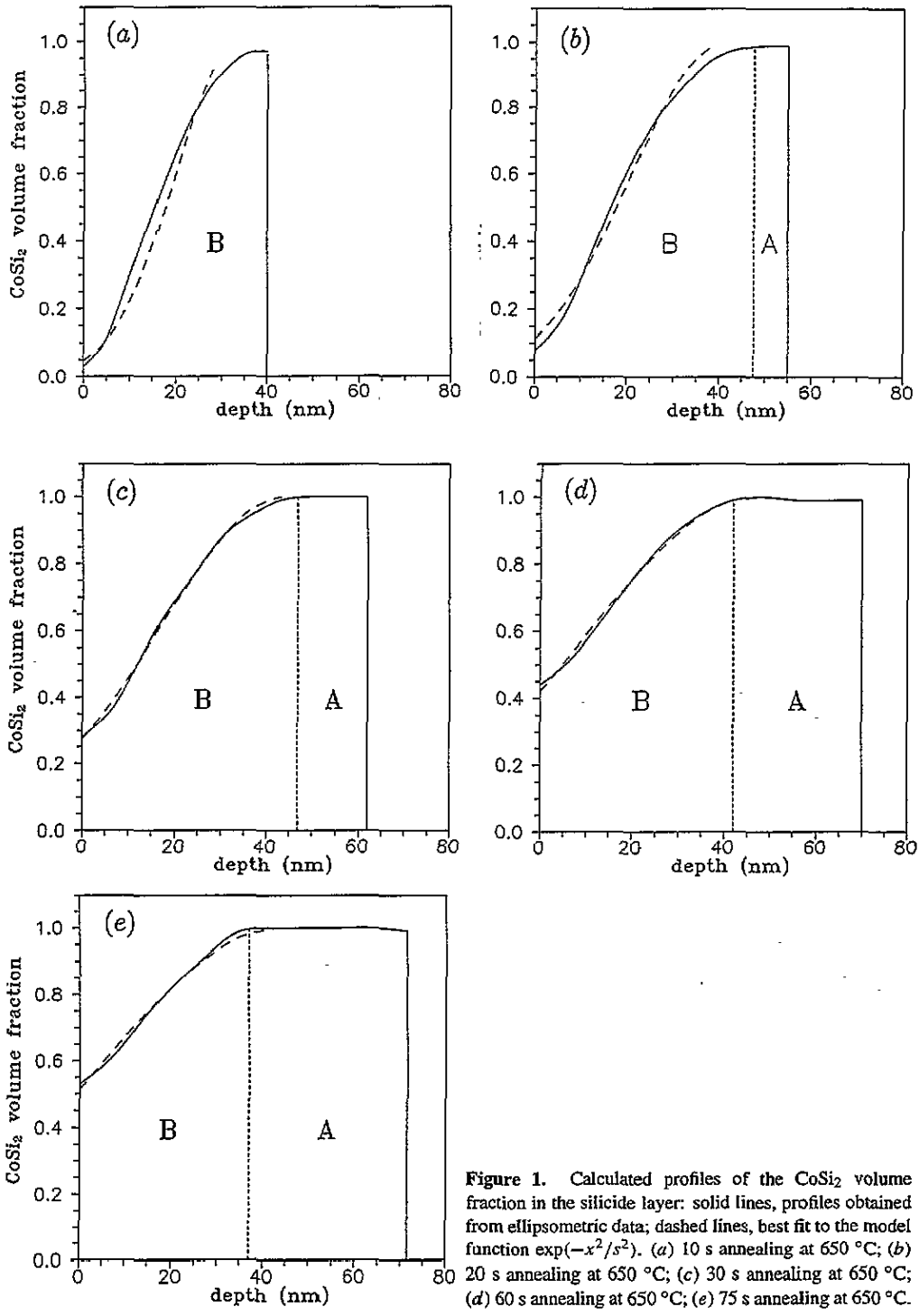

Figure 1. Calculated profiles of the $CoSi_2$ volume fraction in the silicide layer: solid lines, profiles obtained from ellipsometric data; dashed lines, best fit to the model function $\exp(-x^2/s^2)$. (*a*) 10 s annealing at 650 °C; (*b*) 20 s annealing at 650 °C; (*c*) 30 s annealing at 650 °C; (*d*) 60 s annealing at 650 °C; (*e*) 75 s annealing at 650 °C.

It is known [19] that the shape of the profile depends on the distance between the grain boundaries. If this distance decreases and the parameter $\Lambda = L/(D_l t)^{1/2}$ is less than 0.1

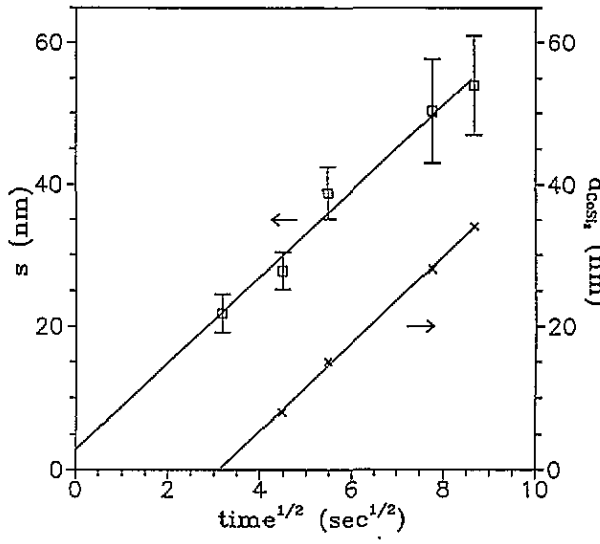

Figure 2. Values of the parameter $s = (4D_bt)^{1/2}$ obtained from the best-fitting procedure (□) and the thickness of the $CoSi_2$ layer (×) versus the square root of the annealing time.

(where $2L$ is the distance between grain boundaries, t is the time), the concentration profile is given by the function

$$C(x, t) = \left[M/(\pi D_b t)^{1/2}\right] \exp(-x^2/4D_b t). \tag{5}$$

Here x is the distance from the substrate toward the surface, the diffusion direction.

From a known concentration profile we could calculate directly the grain boundary diffusion coefficient that characterizes the diffusion process in the material.

We found that function (5) represents well the obtained profiles of $CoSi_2$ distribution in the surface inhomogeneous region. Then we fitted our profiles to the model function

$$q(x) = \exp(-x^2/s^2) \tag{6}$$

by adjusting values of the parameter $s = (4D_bt)^{1/2}$. The fitting procedure minimizes χ^2, given by

$$\chi^2 = \frac{1}{n-m-1} \sum_{i=1}^{n} \frac{[q_{\exp}(x_i) - q(x_i)]^2}{(\delta q)^2} \tag{7}$$

where $q_{\exp}(x_i)$ is the volume fraction of the $CoSi_2$ at depth x_i calculated from ellipsometric data, $q(x_i)$ is the calculated value of the model function (6) at the same point, n is the number of points in depth and m is the number of adjustable parameters.

The obtained model concentration profiles are shown in figure 1 with dashed lines. The values of the function χ^2 resulting from minimization (0.4, 0.45, 0.07, 0.04 and 0.08 respectively) indicate that the fits are consistent with the data within the estimated error limits δq.

Obtained values of the parameter s with corresponding error bounds are shown in figure 2 as a function of the square root of the treatment time. One can see from figure 2

that obtained parameters fit well as a straight line that crosses the y axis close to the origin. The calculated diffusion coefficient is $(1.08 \pm 0.05) \times 10^{-13}$ cm^2 s^{-1}. This result is of the order of the effective diffusion coefficient—1.8×10^{-13} cm^2 s^{-1}—obtained in the paper of Zalkind *et al* [20] for diffusion through the $CoSi_2$ layer, formed during thermal annealing. The obtained profiles of $CoSi_2$ volume fraction could be associated with silicon diffusion profiles in the silicide layer.

It is seen from figure 2 that the two straight lines, representing the increase of the parameter s and the increase of thickness of the $CoSi_2$ layer versus the square root of the annealing time, are nearly parallel.

The fit between the model function (6), representing the grain boundary diffusion, and the obtained $CoSi_2$ volume fraction depth profile is excellent for longer annealing times. This fact is in accordance with the dependence of the shape of the concentration profile on the grain dimension predicted by the theory of diffusion. At the early stages of annealing the diffusion processes are more complicated and the fit between the profile calculated from ellipsometric data and the model function is worse. When the grains of growing $CoSi_2$ become larger, the grain boundary diffusion remains dominant.

Thus, our results show that a diffusion of Si into CoSi along grain boundaries of previously formed $CoSi_2$ is involved in the mechanism of the growth. Probably $CoSi_2$ grows also at the lower and the upper interface by the reaction (i), accompanied by the Co diffusion along $CoSi_2$ grain boundaries toward the substrate.

There is no point in further speculation on the actual diffusion mechanism, because we have no systematic ellipsometric measurements for depth profiling of intermetallic layers and to determine kinetic parameters and the mechanism of phase transformations. The obtained value of the effective diffusion coefficient is in agreement with the results from an *in situ* x-ray diffraction study of silicide formation in the Co–Si system [20].

4. Conclusions

In the present paper it is shown that the ellipsometry is a sensitive tool for studying the phase transformations in the case of intermetallic growth during RTA and could give an insight into the reaction kinetics and mechanisms.

Our algorithm for experimental ellipsometric data interpretation allows us to overcome the parametrization of the inverse problem by the two-layer or multilayer model. It extracts the depth profiles of parameters (optical, structural or compositional) without a knowledge of the concrete mathematical function describing their variation with depth. We use this algorithm for the evaluation of the evolution of the $CoSi_2$ formation with time during RTA at 650 °C. Profiles of the $CoSi_2$ volume fraction with depth of the silicide layer are obtained for different annealing times. The results show that an inhomogeneous layer is forming during annealing where two phases of cobalt silicide ($CoSi_2$ and CoSi) are present with continuously varying ratio with depth. An entirely $CoSi_2$ layer is initially formed on the silicon substrate after 10 s from the beginning of the annealing process and its thickness increases linearly with the square root of the treatment time.

The profiles of the $CoSi_2$ volume fraction in the top inhomogeneous region of the silicide layer are interpreted as resulting from the Si grain boundary diffusion along growing $CoSi_2$ grain boundaries. The grain boundary diffusion coefficient is calculated by fitting the $CoSi_2$ profiles to a model diffusion profile predicted by the theory of diffusion in polycrystalline thin films.

The above results demonstrate the capabilities of the ellipsometric method and our algorithm for experimental data interpretation in a field where ellipsometry has already been used successfully.

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