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An Ellipsometric and RBS Study of $TiSi_2$ Formation

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Abstract

Thin (about 10 nm) titanium layers have been grown on clean Si(111) surfaces inside a UHV system and subsequently heated. The Ti-Si solid state reaction initiated is followed by three-wavelength ellipsometry. Successively we observed two metastable phases at about 350 and 450 °C (states I and II) prior to a final transition at about 700 °C (state III).

The as-deposited layers, the intermediate states I and II, and the final state III have been characterized by means of spectroscopic ellipsometry ($E = 2.0$–4.5 eV). Analysis of state I reveals an inhomogeneous, probably silicon-enriched monosilicide. State II is again homogeneous and it has an almost stoichiometric composition of $TiSi_2$. Most probably it is the C49 disilicide phase. Optical analysis of the final state III reveals a thick layer of C54 $TiSi_2$ islands containing 20%-25% c-Si precipitates.

Reference samples identical to states I, II and III were made and investigated by Rutherford backscattering spectroscopy. Both thickness and composition results obtained from these measurements fully support the results of the ellipsometrical study.

1. Introduction

Until now, the majority of the studies performed by spectroscopic ellipsometry have concerned planar systems of semiconductors and isolators, *e.g.* buried oxide or nitride layers [1-5]. Metallic systems have the disadvantage that the dielectric functions required are not uniquely known [6-9]. In this paper we present such an investigation. Thin titanium layers are grown on a silicon substrate. Heating this system initiates a Ti-Si solid state reaction [10-16].

2. Experimental details

The *in situ* experiments were performed in a UHV system (base pressure 5×10^{-10} Torr) equipped with a titanium evaporation source, an Auger system, an Ar^+ ion gun and a spectroscopic rotating analyzer ellipsometer (RAE) [17, 18] in the energy range 2-4.5 eV.

Heating of the samples was performed by an interactive, computer controlled system. The RAE was completely automated and controlled by an LSI-PDP11 microcomputer [19]. The interactive computer program permitted five options: (1) control of the annealing current, (2) temperature measurement at any moment, (3) spectroscopic ellipsometric scanning from 2 to 4.5 eV over 25 energies, (4) fast (within 30 s) determination of the ellipsometric parameters Δ and ψ at three wavelengths with a precision better than 0.02° for both Δ and ψ and (5) measurement of Δ and ψ at three wavelengths at a number of equal time intervals. The first spectroscopic ellipsometric scan and the first three-wavelength measurements were two-zone measurements [20, 21]. The second and subsequent ellipsometric measurements were single-zone measurements which were corrected by the previously determined two-zone differences. The three wavelengths for the time registrations were chosen so that they provide surface (365 nm) as well as depth information (450 and 550 nm) [22, 23]. The information depth was about 30 nm.

3. Experimental results

About 14 experiments were performed. Figure 1 shows the generally observed changes of Δ and ψ as a function of temperature for a titanium layer of around 10 nm. The transition phases denoted by states I, II and the final state III, were characterized by means of spectroscopic ellipsometry.

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4. Optical analyses

4.1. Intermediate state II

The spectrum of state II has been analysed by means of the method of Arwin and Aspnes [24].

The result of this analysis is displayed in Fig. 2. Our particular interest concerns the pseudodielectric function that exhibits the least c-Si related features. This condition is satisfied mostly for $d = 27$ nm; the curve exhibits the least remnants of the 3.4 eV c-Si peak while the global shape of the curves does not show the onset of the absorbing region of c-Si. From this simple analysis, we may conclude that the layer is homogeneous, otherwise the silicon-related structure could not be eliminated [24], and is about 27 nm thick.

4.2. Intermediate state I

We have applied the same method of analysis to the spectrum of the intermediate state I. The pseudodielectric functions calculated are depicted in Fig. 3. Studying the real part, one sees that it has an S-like shape for $d = 18$, 19 and 20 nm, which correlates with the dielectric function of c-Si. This shape and the feature at $E = 3.4$ eV cannot be eliminated at the same time. The same problem appears in the imaginary part of the spectrum. Apparently we do not have a homogeneous layer; nevertheless, the silicon-related features are minimized for $d = 19 \pm 0.5$ nm, showing that although the layer is inhomogeneous, it has a thickness of approximately 19 nm. A possible explanation is obtained from the work of Raaijmakers [16], who has made Auger electron spectroscopy (AES) depth profiles of similar layers, revealing a large concentration gradient for silicon.

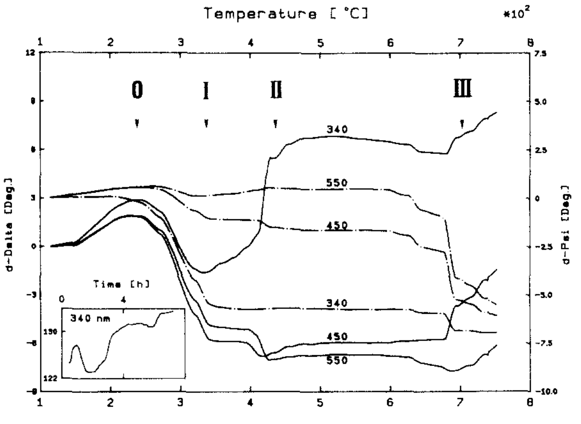

Fig. 1. The changes of Δ (solid lines) and ψ (broken lines) upon heating. The inset shows $\delta\Delta_{340}$ as a function of time. The arrows indicate intermediate states.

4.3. The as-deposited layer

From previously published studies on interface formation at room temperature it is known that a Ti–Si intermix at the interface and a thin (2–4 nm) TiSi transition layer are formed that are subsequently overgrown by pure titanium [25–27]. We have the dielectric functions of titanium and c-Si at our disposal [8, 9, 28], and if there is an intermixed region formed it should be like state I. Hence, we have both dielectric functions involved at our disposal, and therefore can apply linear regression analysis (LRA) to compare a number of optional models.

In Table 1 we present the different models and the results. In the first one we have optimized the thickness of a pure titanium layer on a silicon substrate. A substantial improvement is obtained once the titanium layer is allowed to contain voids reflecting the titanium microstructure [6, 9];

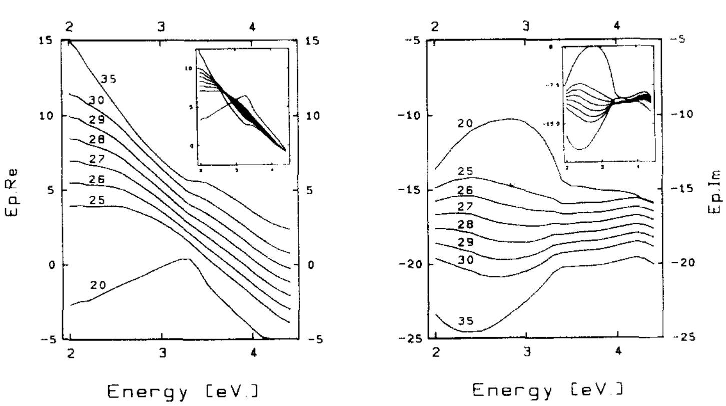

Fig. 2. The pseudodielectric functions of intermediate state II as calculated for several thicknesses. The spectra are shifted to improve the presentation of the c-Si related structure. The insets show the unshifted spectra.

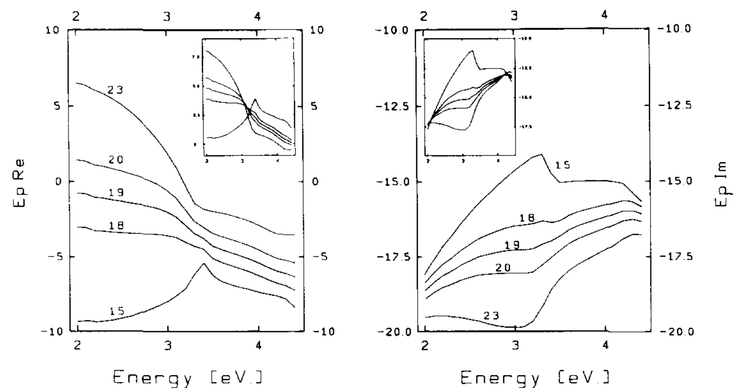

Fig. 3. The shifted and unshifted (insets) pseudodielectric functions of intermediate state I.

TABLE 1 **Results of the LRA of the as deposited titanium layer (Fig. 4)**

Model	*Mixed layer*		*Titanium layer*		*Residue*
	d (nm)	*Void fraction*	*d* (nm)	*Void fraction*	
a	—	—	11.5 ± 0.4	—	3.1×10^{-2}
b	—	—	11.0 ± 0.1	0.11 ± 0.005	8.5×10^{-3}
c	7.5 ± 0.6	—	6.0 ± 0.4	—	7.0×10^{-3}
d	3.9 ± 0.3	0.28 ± 0.08	8.4 ± 0.3	0.04 ± 0.015	3.5×10^{-3}
Average	3.3 ± 1.3	0.25 ± 0.2	—	0.05 ± 0.10	3.2×10^{-3}

The uncertainty limits are listed behind the optimized values. The last row presents the average results and their standard deviations of the 14 experiments performed.

the residue becomes 8.5×10^{-3}, which for the case of this kind of analysis becomes an acceptable fit [1–5]. These voids are incorporated by means of the Bruggeman effective medium theory [29–31]. However, our main interest concerns the existence of an intermixed layer. For this purpose, we have fitted the experimental data to two models: (1) a coarse model with two layers of pure components, the top titanium and the second layer like state I and (2) a more advanced model with two layers of variable thicknesses and void fractions. In both cases the fits obtained have improved, see Table 1. The confidence limits remain small, showing that the presence of an intermixed layer can be unambiguously established.

4.4. Final state III

Application of the method of Arwin and Aspnes to spectrum III does not yield a dielectric function that lacks all c-Si related features. Moreover, it shows that the c-Si peak at 3.4 eV has shifted to a lower energy, which signifies a lattice expansion of the silicon [32–34]. Apparently, silicon crystallites have grown within the top layer and stress is introduced within these grains upon cooling.

We now have some idea of the layer composition, and we can utilize LRA to quantify the layer. The silicon can occur as an overlayer, burying the silicide layer beneath, or it may be found as small crystallites within the silicide layer. Both problems are tackled by a two-layer model. The top layer contains only pure c-Si while the second layer contains three components, *i.e.* $TiSi_2$, c-Si and voids. The dielectric function of $TiSi_2$ is independently determined from a thick co-sputtered and annealed $TiSi_2$ layer. This model should discriminate between a c-Si overlayer and a silicide layer containing c-Si precipitates. We have shifted the dielectric function of c-Si of the layers in order to meet the lattice expansion. The results of these analyses exclude the c-Si overlayer; they reveal a thick (80 nm) $TiSi_2$ layer containing 24% c-Si and no voids. The value for the thickness is of no relevance since the information depth has been surpassed.

5. Reference samples I, II and III and RBS measurements

The *ex situ* study of the intermediate states I and II of silicide formation that we have distinguished requires a number of carefully pre-

TABLE 2 Comparison of samples I and II with the metastable phases I and II

Sample	*Top layer*		*Second layer*		*Residue*
	Thickness (nm)	*Void fraction*	*Thickness* (nm)	*Void fraction*	
I	3.0 ± 3	0.02 ± 0.1	15.7 ± 3	0.05 ± 0.01	0.005
II	1.8 ± 3	0.10 ± 0.1	25.2 ± 3	0.00 ± 0.01	0.003

A two-layer model where both layers are allowed to contain a variable amount of voids is used.

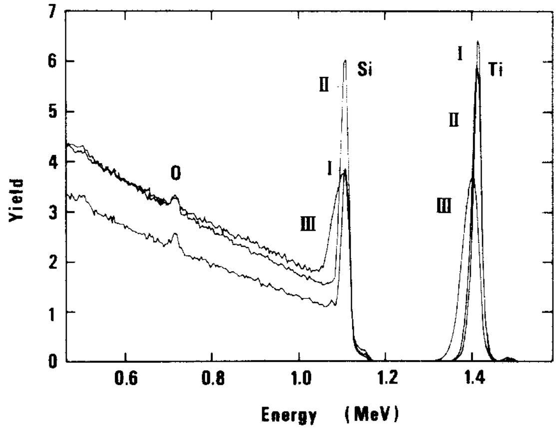

Fig. 4. The RBS spectra for the reference samples I, II and III.

TABLE 3 The composition and thickness of the silicide layers of samples I, II and III

Sample	*Silicide layer*	
	d (nm)	*Atomic ratio* $N_{Si}:N_{Ti}$
I	20	1.2
II	25	2.1
III	50	2.35

pared samples which are equivalent to these intermediate states. The sample discussed in the optical analyses provides us the final state sample, sample III. The samples identical to the metastable phases I and II had to be prepared.

Table 2 shows the optical analyses of the references samples I and II. A two-layer model where both layers are allowed to contain a variable amount of voids is used. The residues of both fits are extremely low, showing that the dielectric functions used are the appropriate ones, and we can safely conclude that samples I and II are identical to the intermediate states I and II as observed during the annealing of sample III.

Samples I, II and III were investigated by means of RBS [35]. The experiments were performed with a 2 MeV helium ion beam at normal incidence and at a scattering angle of 170°.

Figure 4 displays the RBS spectra as they were recorded for the three samples. The spectra were analyzed by the simulation program RUMP [36]. With regard to the samples I and II, a single layer containing silicon, titanium and oxygen sufficed to simulate the spectra. In case of sample III, two layers were needed, a SiO_2 layer above a Si–Ti layer. The results are shown in Table 3. The shape of the RBS peaks of sample III has become asymmetric, showing that the layer is not as flat as those observed for samples I and II. The amount of silicon in the layer as it emerged from the optical analysis is slightly larger than the present result.

These and the previous optical results which revealed c-Si precipitates suggest that the heating at 700 °C has probably yielded a top layer of large, flat $TiSi_2$ crystals embedded in a c-Si matrix.

6. Discussion

The conversion from the as-deposited layer to state I is accompanied by a volume expansion. The expansion can be calculated from the thickness of the initial titanium layer and that of the finally obtained intermixed layer. We have found that 1 nm of titanium eventually yields 2.1 nm of state I material. In the literature it is reported that the formation of 2.7 nm of $TiSi_2$ requires 1 nm of pure titanium, *i.e.* a volume expansion of 2.7 [10]. Hence, state I is most probably silicon enriched TiSi. This conclusion is fully confirmed by the RBS analysis of sample I.

At about 450 °C, a homogeneous phase (II) is formed. The volume expansion occurring in the formation is slightly less than 2.7. Apparently we have obtained $TiSi_2$. However, the temperature of formation is too low to permit the formation of the C54 structured $TiSi_2$ and thus a C49 structure is expected [16]. Again, we have found excellent agreement between the optical analysis and the results of the RBS measurements.

A final transition is observed at about 700 °C and a stable layer is obtained. The layer is composed of C54 $TiSi_2$ crystallites and contains about 25% of c-Si precipitates. The presence of these c-Si precipitates and the observed surface roughening clearly shows that substantial recrystallization is involved in the transition.

7. Conclusions

In this paper we have reported on a study of the Ti–c-Si solid state reaction. Two techniques have been applied: spectroscopic ellipsometry and RBS. The results obtained from both techniques are in excellent agreement with one another.

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