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Résumé - La caractérisation de couches de TiN sur Si monocristallin, obtenues par implantation ionique, a été effectuée en traitant les mesures ellipsométriques par un programme très souple qui s'adapte bien aux conditions expérimentales. Les résultats obtenus sur les couches implantées et recuites par faisceaux d'énergie (faisceau d'électrons, lumière incohérente) sont examinés en vue d'applications technologiques possibles.

Abstract - The optical characterization of TiN films produced on Si substrates by ion-implantation was performed by handling the ellipsometric measurements through a flexible program which well conforms to the various experimental situations. The results obtained on as-implanted and transient thermally annealed films are discussed in relation to different possible technological applications.

1. INTRODUCTION

Bulk Titanium nitride (TiN) is a very stable compound (M.P. 2930°C), characterized by an electrical resistivity ($22\mu\Omega\cdot$cm) lower than that of metallic Ti. The employment of TiN in thin film form as conductive layer and diffusion barrier in semiconductor technology was described as early as in 1969 /1/: since then, much work was performed in this field, with a number of interesting achievements /2-6/.

However, little work has been so far reported on the feasibility of TiN-based transparent conductive films for silicon solar cells /7/: this is due to the fundamental difficulty of obtaining a good compromise between good optical and electrical properties, which are differently related to stoichiometric deviations and impurities content. We adopted a preparative technique based on ion-implantation of Nitrogen onto a Silicon wafer coated with a layer of metallic Ti /8/.

For optical characterization we exploited the ellipsometric technique, supported by a proper computer program , able to deal with considerably absorbing films: in this work the strategies of such a program are described in detail, together with some applications to ion-implanted TiN films, subsequently annealed by different transient thermal procedures.

2. COMPUTER MODEL

A brief account of the model has been given in /9/. Here we recall the main features of the code as well as the improvements with respect to the previous version described in details in /10/. The program has been named ROSALBA; this name will be used in the following as a shorthand. ROSALBA is able to deal with systems containing one or more thin absorbing layers deposited on a substrate, however the inversion procedure may be applied only to one film at a time, all the others parameters being held constant. The code determines simultaneously the unknown parameters n, k, d, in a variety of experimental situations, which can be grouped into two categories : two (Ψ,Δ) measurements sets or one (Ψ,Δ) measurement set plus the experimental reflectance. The adopted numerical procedure is based on a series of successive interpolations in the three-dimensional (n,k,d) space. Such a strategy may appear as quite naïve, however it allows one to control step by step the search for the solution, so that problems arising from multiple and/or physically meaningless solutions are avoided. Moreover it should be noted that different initial estimates of the range in which the unknown parameters are supposed to lie, as well as the increments

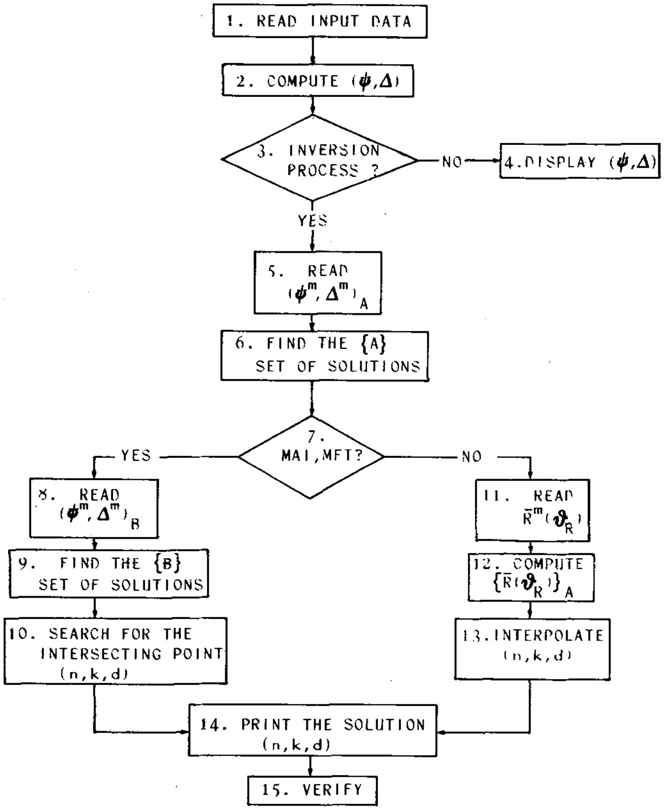

Fig. 1 - Schematic flowchart of the ellipsometric programme ROSALBA.

chosen of n, k, d (see below) do not affect the uniqueness of the solution.

The flowchart scheme of ROSALBA is shown in Fig. 1, which must be read as follows.

Box 1. The program reads the input data: i) number of phases of the system; ii) n,k,d of all but one phase; iii) the range of values of the unknown n,k,d for the layer under investigation; iv) the wavelength λ and the incident angle ϑ.

Box 2. Via the 2x2-matrix method for multilayered structures /11/ a set of (ψ,Δ) as a function of n, k, d is obtained for further use. n, k, d range in the $\{n\},\{k\},\{d\}$ arrays respectively, in which the unknown n, k, d are supposed to lie.

Box 3. If the inversion process is required the control is transmitted to Box 5, otherwise to Box 4.

Box 4. ROSALBA displays ψ and Δ as a function of the input data. Such a display may be useful for: i) determining more exactly the $\{n\},\{k\},\{d\}$ arrays; ii) choosing the best working conditions. In fact, by treating the simulated ψ and Δ values as experimentally observed values, it is possible to evaluate the sensibility of different experimental arrangements.

Box 5. If the inversion process is needed, the code reads the set of measurements $(\psi^m, \Delta^m)_A$.

Box 6. For each value of k in $\{k\}$ the program interpolates in the set of computed (ψ,Δ) every possible solution corresponding to the experimental $(\psi^m, \Delta^m)_A$. So that at the end of this part of computation we find a set of solutions A_1, A_2, ... A_j .. call it $\{A\}$, with:

$$A_j = \{n_A{}^j,\ k_A{}^j,\ d_A{}^j\}.$$

If d is known, by an independent measurement, the final solution is determined by computing the interpolated values of n and k corresponding to d.

Box 7. If d is unknown, to determine the three unknown parameters simultaneously it is necessary at least another ellipsometric measurement (Box 8) or a photometric measurement of the reflectance (Box 11).

Box 8. With a second set of experimental data $(\psi^m, \Delta^m)_B$ the above calculation is repeated. The numerical procedure for determining the solution is independent of the employed method: i) multiple-angle-of-incidence (MAI), ii) multiple-film-thickness (MFT) /12/.

Box 9. The $\{B\}$ solutions are determined.

Box 10. In the (n,k,d) space $\{A\}$ and $\{B\}$ solutions generate two curves and the program searches for their intersection which yields the value of the unknown parameters.

Box 11. The program reads the experimental reflectance $\bar{R}^m(\vartheta_R)$. The angle ϑ_R at which the reflectance is measured may be different from the angle of incidence ϑ with respect to the geometry of analysed systems.

Box 12. For each A_i the reflectance $[\bar{R}(\vartheta_R)]_i$ is calculated.

Box 13. The solution is determined by computing the interpolated values of n, k, d corresponding to $\bar{R}^m(\vartheta_R)$.

Box 14. The solution determined according to one of the described procedures is printed.

Box 15. Whichever way is followed, the obtained values of n, k, d are reinserted in input to calculate the corresponding ψ and Δ, call them ψ^c, Δ^c. The differences $|\psi^c - \psi^m|$ and $|\Delta^c - \Delta^m|$ represent the errors due to the whole mathematical procedure. These errors must be smaller than the experimental errors in ψ^m and Δ^m.

ROSALBA needs a quite contained computer time. If one uses 20 steps in each of the $\{n\}$, $\{k\}$, $\{d\}$ arrays, it is necessary ~3 sec of CPU to find the solution by applying MAI or MFT method with the Cyber 70/76 CDC System.

3. EXPERIMENTAL

Metallic Titanium 70 nm thick films were evaporated onto (100) silicon substrates and then implanted by 40 keV N_2^+ ions, reaching a final dose of 4.3×10^{17} atoms/cm^2. Due to the very high implanted dose of Nitrogen that requires a long time even with the 4 mA current supplied by our Lintott III implanter, the TiN films thus obtained were found to be covered by a 30 nm Carbon layer, which was removed by ion beam etching. Thermal treatments were performed to reach a good homogeneity of the films, a lowering of the absorption and a higher conductivity. To keep low the Oxygen contamination due to the annealing, these treatments were performed via the unconventional transient methods obtained by electron gun and incoherent light flashes coming from a high power Xe lamp. The temperatures reached by the samples during electron beam annealing were 600, 700 and 800°C for about 5 seconds, while during incoherent light were nearly 800°C for about 14 seconds.

The films were electrically characterized through resistivity measurements performed using the four-point probe and van der Pauw methods. The thickness of some samples were tested by Talystep.

The optical characterization was performed by ellipsometry, using a Gaertner L-119 instrument, working with the green line of a Hg lamp (λ=546 nm). The whole alignment procedure was performed with all optical elements inserted (polarizer, analyzer, compensator) to bypass the problem of the non-parallelism of the faces of one of them, namely the compensator; in fact we judged incorrect to follow an alignment procedure without the compensator, that modifies the lateral and vertical displacement of the beam when positioned in C^+ or C^- /11/. Due to this problem, all the measurements were "two zones", with the compensator set at C^- at the beginnning and no more removed. Several angles of incidence were used, varying from 60°to 78°.

4. RESULTS AND DISCUSSION

All the results obtained for optical and electrical measurements are shown in Table I; we report the following observations:

a) the optical constants of the samples T1, X1 and X2 were obtained by using both the ellipsometric measurements and the Talystep evaluated thickness, owing to the high in-depth inhomogeneity of the films. The optical constants obtained are therefore the integrated ones, in agreement with the relation /13/:

$$\langle\tilde{n}\rangle = \frac{1}{d}\int_0^d \tilde{n}(x)\,dx .$$

b) The optical parameters of the other samples were obtained through MAI measurements and each represents the average (with relative standard deviation) of 8 couples of values taken at different angles of incidence. We note that, due to the low dependence of ellipsometric measurements from the angle of incidence, the (n,k) curves obtained by MAI evaluations, as it's well known, may be not enough resolved. Anyway the computer program can find a mathematical intersection, but the experimental errors have a very large influence on it. However, if one performs several ellipsometric measurements at more than two angles of incidence, the average values of all intersections may give, also in this case, acceptable results.

TABLE I
Optical and electrical properties of ion-implanted TiN films on Si.

Sample	Annealing	Temper. (°C)	n $\Delta n.10^{-2}$	k $\Delta k.10^{-3}$	d(nm)Δd	$\rho(\mu\Omega.$ cm)
T1	--	--	1.77 (7)	0.640 (30)	105 (5)	284
G1	el. beam	600	1.72 (1)	0.529 (4)	100 (1)	177
G2	el. beam	700	1.69 (2)	0.517 (6)	102 (2)	119
G3	el. beam	800	1.58 (2)	0.519 (6)	101 (2)	32
X1	inc. light	800	2.15 (5)	0.140 (20)	82 (5)	254
X2	inc. light	800	2.16 (5)	0.070 (20)	82 (5)	205

Δn, Δk, Δd are standard deviations

5. CONCLUSIONS

By means of a flexible computer program , we were able to treat successfully various aspect of the complex problem to elaborate ellipsometric measurements of even not transparent films deposited on absorbing substrates. Moreover, it is worthwhile to point out that this program can handle data coming from samples not especially prepared, but in any case encountered in experimental practice, whose optical parameters and thickness do not therefore maximize the sensitivity of the procedure.

As regards technological applications, after incoherent light annealing performed in air, the optical properties become interesting, accounting also for the fairly low resistivity, for photovoltaic applications on Silicon solar cells. On the other hand, after electron beam annealing, the optical parameters are not satisfactory for this purpose, but, owing to the very low resistivities so obtained, this treatment appears suitable for films to be employed as interconnections and/or diffusion barriers in microelectronics.

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