Bulgarian Chemical Communications, Volume 45, Special Issue B (pp. 51-54) 2013

UV and NIR optical functions of very thin (< λ / 50) Hf, Al or Ti doped tantalum pentoxide films, deposited on Si [100] substrate

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Received October 17, 2013; Revised November 25, 2013

We study the optical characteristics of tantalum pentoxide films, deposited on Si [100] substrate by reactive sputtering. These films are investigated as high-kappa materials for the needs of nano-electronics, i.e. design of DRAM. Metal oxides are thermodynamically unstable with Si and an interfacial layer is formed between the oxide film and the silicon substrate during the deposition process. The physical situation gets more complicated when the Ta_2O_5 layer is doped – the overall structure becomes non-homogeneous. Herein, we study the optical properties of Ta_2O_5 layer deposited on Si substrate and doped with Hf, Al or Ti. The evaluation of the optical parameters of the structure is fulfilled with the genetic algorithm approach from spectral photometric measurements. The overall physical thickness of the structure, assumed to be equivalent to 3 homogeneous layers and the equivalent refractive indices of each layer are estimated from 240 to 750 nm.

Keywords: High-kappa materials, Non-homogeneous thin films, Optical functions

INTRODUCTION

Modern electronics till recently was based on SiO_2 devices which have reached the limits of miniaturization due to quantum mechanical effects at 1 – 2 nm thickness. New advancing replacements of SiO_2 are the so-called high-permittivity (high-kappa) materials, which already have found applications in next-generation dynamic random access memories [1]. Metal oxides (Ta_2O_5, HfO_2, ZrO_2, etc.) are investigated intensively because their high-kappa is leading to higher physical thickness. Thus, the effective thickness of the oxide is less than 1 nm. Pure and doped Ta_2O_5 thin films are promising candidates for next generation nano-electronics devices [3].

Unfortunately, there are two facts that make the optical characterization of metal oxide films on Si very difficult. First, their optical properties are tightly correlated with the layer synthesis conditions, i.e. layers show different exponential absorption in the sub-gap spectral region. Second, metal oxides are thermodynamically unstable with Si [2]. An interfacial layer (IL) is formed between the oxide film and the silicon substrate during the deposition process. That affects directly the performance of the active nano-electronic devices. Herein, studies are presented on the characteristics of very thin (1 to 10 nm) Ta_2O_5 layers doped with Hf, Al or Ti. The physical situation gets more complicated, because the doped Ta_2O_5 layer becomes non-homogeneous.

The optical functions of Ta_2O_5 have been studied systematically for the last 10 years [3]. Different models of the oxide permittivity have been tried, i.e. Sellmeier, Lorentz, Forouhi – Bloomer, etc. [See Ref. 6 and references therein]. One of the latest (and very successful) is the extended Tauc – Lorentz model (suggested by Jellison and Modine) with Urbach tail absorption law for the sub-gap region (T-L-U). As a rule, thick samples (70 – 200 nm) are investigated and spectral ellipsometric data is used for the fitting procedure, based on Levenberg – Marcquardt (L-M) derivative method [3, 4]. The interfacial layer usually is described in the effective medium approximation, although a direct approach based on ideas for solving ill-posed inverse problems is also proposed [3]. Recently we have determined the optical functions of non-doped Ta_2O_5 on Si [100] and the parameters of the IL layer [5, 6].

The aim of this work is to extract from spectral photometric data the optical characteristics of Si/IL/doped-Ta_2O_5 structure, which is assumed as a stack of 3 homogeneous layers on a Si [100]

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substrate. Reflectance at nearly normal incidence is measured between 240 and 750 nm. Model parameters are estimated by the help of stochastic genetic algorithm [6]. The Si, SiO_2, and the metal oxides HfO_2, Ti_2O_3 и Ta_2O_3 optical functions are taken from literature [4].

EXPERIMENTAL

Tantalum pentoxide thin films (provided by ISSP - BAS [1] see Acknowledgments) were deposited on chemically cleaned p-type 15 Ω.cm Si [100] wafers (after HF last pre-clean to remove the native oxide layer). No deionized water rinse was used in an effort to minimize the formation of a new oxide film. Films with thicknesses of 5 to 16 nm were deposited by reactive sputtering of Ta target (purity of 99.99%) in Ar and 10% O_2 atmosphere. The working gas pressure was 0.33 Pa, rf power density - 3.6 W/cm^2, and the substrate temperature during deposition was 200 ^oC. Previously, it was found [1] that high quality layers can be obtained by rf sputtering. These optimized conditions were applied for deposition of the Ta_2O_5 films studied here with respect of their optical parameters. The doping was done by deposition of a thin metal film on the top of the Ta_2O_5 layer. Post deposition annealing was performed in N_2 at 400 ^oC for 30 min. Reflectance spectra were measured with high precision Cary 5E spectrophotometer at nearly normal incidence (light incidence at ~8 degrees, TM polarization) in the range 240 - 750 nm with experimental uncertainty of 1% to 0.5%.

RESULTS AND DISCUSSION

We consider a simple model of 3 layers on Si [100] substrate. The layers are assumed as homogeneous with no roughness. The first layer next to the substrate is IL with unknown physical thickness. For the doped Ta_2O_5 films we assume an equivalent 2 homogeneous layers structure. That assumption is based on Herpin theorem for non-homogeneous films. The refractive index and thickness of every layer are unknown. Generally, the optical characterization of thin films is based on least square fits to experimental data. These fits are mathematical procedures in order to solve a set of non-linear equations in the presence of inevitable experimental uncertainties (errors). The search for a solution (numeric fitting) is obtained by different minimization techniques. In the present study, we used several derivative approaches (L-M included), but the results were unstable with strong dependence on the initial guess. It is not obvious that fitting procedures that are successfully applied to films with physical thickness D > 50 nm, are effective for very thin layers, when $D < \lambda/60$, (λ is the wavelength). Besides, the derivative methods use one point in the parametric space for determination of step magnitude and direction to the global minimum, while stochastic algorithms start with a set of possible solutions and new set is generated at each new iteration. That is why we preferred for evaluation of unknown parameters the so-called genetic algorithm (GA), which has a stochastic nature.

There are three substantial steps in GA: initiation, evolution, and termination [5]. First stage is a choice of 'initial population': points in the parameter space of the fitting model. This population has 'aim and aspiration': to find a global minimum of the objective function in the parameter space within the termination limits. The aim is reached after several 'generations' of the initial population by evolution and reproduction. The algorithm makes 'evolution' by selection rules (roulette, tournament, etc.). 'Reproduction' is done by crossover and mutation. It is obvious that the mathematics behind these intuitive descriptions is very complicated. From User point of view, the problem is that there are over 30 parameters of the algorithm to be tuned before the start of the procedure in order to obtain a robust estimation of the unknown parameters. Here we give some specific features of the GA procedure. We chose 100 'generations' to reach the global minimum, each one with a 'population' of 120 'individuals', members of 3 'tribes'. Migration between the tribes was allowed in both directions. The crossover fraction was 0.6 and the selection rule was set to the type 'roulette'. The minimization procedure is terminated if the maximum number of generations (100, in this search) is exceeded.

The implementation of the GA method for fitting procedures to IL/Ta_2O_5 reflectance data (R) had two supplementary features. First, we found that there is a strong statistical correlation between the model parameters. That is why the oxide film physical thickness D is uncoupled from GA fitting. An internal loop (step 0.1 nm) for D is organized. New GA procedure is launched at each thickness iteration. Second, in order to eliminate a lot of 'white or coloured' noise in the fitting procedure, minimization is done in a certain spectral sub-region. In the limit $D/\lambda \to 0$ (for λ in VIS and NIR in this study), the film optical response becomes less sensitive to variations of the unknowns. The choice of this spectral sub-region is rather arbitrary and based on “trial and error” approach. The results presented below are obtained with GA fitting for wavelengths between 236 and 380 nm. The estimated model parameters from the spectral sub-region are used to calculate the optical response in the whole experimental spectral region (extrapolation in UV and NIR), which are then compared to the experimental data from 240 to 750 nm.

We found that GA approach, being intrinsically non-derivative method, has certain advantages compared to L-M in this case. The key issue is to have over-determined set of non-linear equations as possible. The last is true if, *and only if*, variations of a model parameter lead to a perceivable change in the optical response [5-6]. That is why, in what follows below, we restricted the spectral range of the fitting between 236 and 380 nm.

In Fig.1, the reflectance of the tantalum pentoxide samples on Si substrate is presented, together with the optical response of Al, Hf and Ti doped layers.

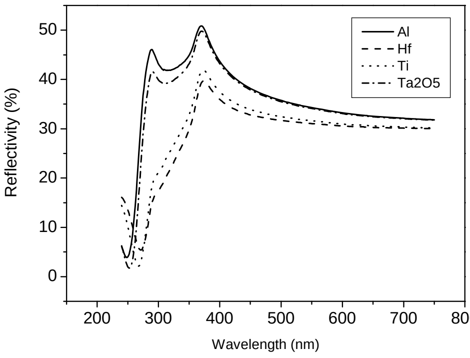

Fig. 1. Reflectivity of pure and doped Ta_2O_5 thin films.

For evaluation of the fitting, we use the root mean square uncertainty (RMSU), normalized by the number of degree of freedom so that it gives the uncertainty (error) per one point of observations. It is a statistical measure of the goodness-of-fit and is compared to the experimental uncertainty. RMSU is calculated by the residuals, defined as difference between the measured data (R) and predicted response by the help of the estimated model parameters.

In Figure 2, 3 and 4 we present the residual of the fits for the Al, Hf and Ti doped Ta_2O_5 thin films. Compared to the uncertainty of the experiment, we can accept the fits as very good.

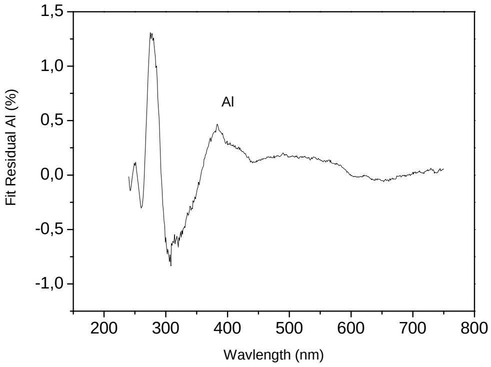

Fig. 2. Residuals of the fit of Ta_2O_5 thin film doped with Al.

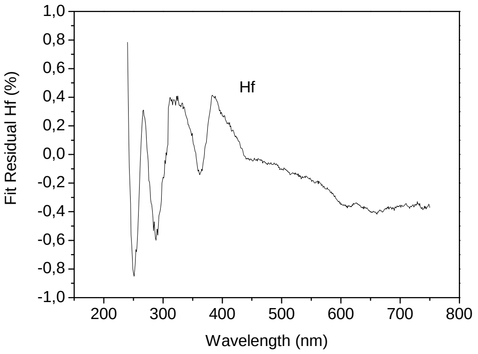

Fig. 3. Residuals of the fit of Ta_2O_5 thin film doped with Hf.

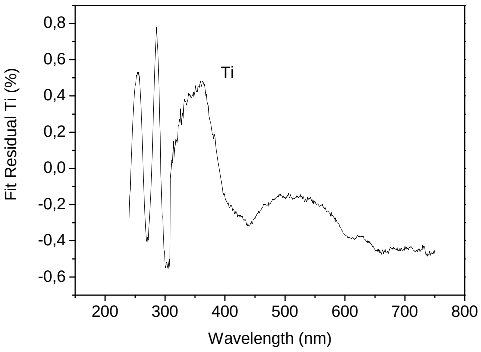

Fig. 4. Residuals of the fit of Ta_2O_5 thin film doped with Ti.

Although the goodness-of-fit criteria is quite convincing, we have to discuss the uncertainties of the estimated parameters. We have calculated the Jacobian at the point in parameter space, corresponding to the global minimum found by GA. Also, we have used a Student’s coefficient of 0.10 and calculated confidence intervals of the estimated parameters. The physical thickness of the Interfacial Layer is in the [1, 1.5] nm interval. The uncertainties of the equivalent homogeneous films are in the range [2, 2.5] nm and the equivalent thicknesses are between 7 and 10.5 nm.

CONCLUSION

Within the simple model of three homogeneous films on Si (100) substrate, we have determined the optical characteristics of doped Ta_2O_5 thin films. In the regression procedure we used three layers model. The layers are assumed as homogeneous with no roughness. We have applied the genetic algorithm in the evaluation of the unknown parameters. This approach is found to be very robust and effective.

Acknowledgments:*The work was financially supported by the BNS Fund (project DTK02/50).*

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Оптически функции в UV и NIR на много тънки (< λ / 50) слоеве танталов петоос, дотирани с Hf, Al или Ti, и отложени върху подложки Si [100]

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Постъпила на 17 октомври 2013 г.; коригирана на 25 ноември, 2013 г.

(Резюме)

Изследвали сме оптическите характеристики на слоеве от танталов пентоокис, отложени върху Si (100) подложки. Ta_2O_5 е представител на хай-капа (high-kappa) материалите, които са най-переспективни за развитието на нано-електрониката. Съществен проблем при дизайна и производството им е, че металните оксиси са термодинамично нестабилни към Si. Това води до получаване по време на техния синтез на нежелан слой 1 – 2 нм на границата между подложката и хай-капа филма. Ако Ta_2O_5 слоевете се дотират, структурата като цяло става нехомогенна, но електическото ѝ поведение се подобрява. Тук разглеждаме оптическите свойства на Ta_2O_5 слоеве, отложени върху Si подложки и дотирани с Hf, Al и Ti. Слоевете са изследвани спектрофотометрично в областа 240 – 750 нм, а измерванията са интерпретирани чрез решаване на обратната оптическа задача с помоща на Генетичния Алгоритъм.