Multilayer silicon rich oxy-nitride films characterization by SIMS, VASE and AFM.

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Abstract. In this work secondary ion mass spectrometry (SIMS), variable angle spectroscopy ellipsometry (VASE) and atomic force microscopy (AFM) are used to investigate the structure, composition and morphology of multilayer SRON films. Three/four SRON sequential layers were deposited on silicon wafers by PECVD and silicon, nitrogen and oxygen content was varied by changing the N2O/SiH4 ratio. The total thickness of the resulting SRON stack is about 50nm. SIMS analyses of NCs+, OCs+, SiCs+, in MCs+ methodology are performed by a Cameca SC-ultra instrument. Depth profiles are obtained at 500eV of primary beam impact energy with sample rotation. An approximate method to obtain silicon concentration is used. Total layer thickness are obtained from both SIMS and VASE measurements. In addition, we compare the thickness of the single layers obtained from VASE with the SIMS depth profiles. A detailed analysis of films morphology is obtained by AFM. The SRON stack is sputtered by SIMS until a certain layer is exposed, which is then analyzed by AFM. The sputtered layers are then etched in HF solution to better resolve the exposed nano-crystals.

1. Introduction
Multilayer silicon rich oxide films (SRO) or silicon rich oxy-nitride (SRON) films are attractive for their application in opto-electronic devices [1]. The electro-optical characterization of the devices has to be correlated to the compositional structure of the films, in order to improve the fabrication process and as ultimate goal to enhance the device efficiency. These multi-layers SRON stacks can be incorporated in MOS structures to obtain LEDs.

Silicon quantification in SRON by SIMS analyses is not a trivial task because of matrix effects. SIMS analyses are affected by sputtering rate variations and ion yield changes throughout the various layers. An approximate method is here adopted to quantify silicon in atomic concentrations, as proposed by the same authors in a previous publication [2]. AFM can provide detailed information about the morphology of the nano-crystals. In particular the structures embedded in a particular SRON layer can be revealed after SIMS sputtering process and etching in HF solution.

Spectroscopic ellipsometry was used by different groups to investigate dielectric matrices (SiO2 or Si3N4) containing Si-nanocrystals either to establish the thickness of the layer(s) containing Si-nano-
crystals and/or to evaluate the dielectric constants of the films [3,4]. The analysis of the ellipsometric spectra of annealed SRO is complicated due to the peculiar properties of the film, which consists of 2 phases, the dielectric matrix and the embedded Si-nanocrystals. Generally, the matrix can be considered as SiO$_2$ with some percent of nitrogen (depending on the film fabrication technique). In our case the films are obtained by fabrication of PECVD deposited SRO and not necessarily the separation into a SiO$_2$ and Si-nc phase is complete, therefore the matrix might also contain some excess Si. While the modeling of the dielectric function of the matrix is complicated due to the excess-Si, the modeling of the Si-nc phase is complicated due to the size distribution of the Si-nanocrystals and quantum-confinement effects resulting in dielectric functions, which differ considerably from the ones of c-Si. Aim of the VASE analysis was to establish total film thickness, the thickness of the sublayers and the refractive indices for comparison with silicon content from the SIMS depth profiles.

2. Experimental

The samples are composed of 3 or 4 silicon rich oxy-nitride (SRON) layers deposited by plasma enhanced chemical vapor deposition (PECVD) on p-type <100> silicon wafers. The layers composition is mainly established by the term $\Gamma$, which defines the N$_2$O to SiH$_4$ ratio during each layer deposition. Lower $\Gamma$ means high silicon excess compared to stoichiometric SiO$_2$. $\Gamma$ can be varied layer by layer in order to obtain a silicon content gradient. Moreover in the layers indicated with N the nitrogen content was changed with 40sccm of NH$_3$ added during the deposition process. Nano-crystals formation occurs during high temperature annealing performed at 1050 °C for one hour. During annealing the SRO stack was protected by a SiO$_2$/Si$_3$N$_4$ layer deposited by LPCVD. This diffusion barrier was removed by dedicated wet-etching processes.

A stoichiometric SiO$_2$ layer deposited on silicon crystalline wafer was used as reference sample for SIMS, for the successive Si quantification in atomic concentration [2].

The SIMS measurements were carried out by a Cameca SC-ultra magnetic sector instrument, with a Cs$^+$ primary beam and monitoring MCs$^+$ secondary ions (where M indicates $^{16}$O, $^{14}$N or $^{28}$Si respectively). MCs$^+$ molecular signals were normalized point by point to Cs$^+$ secondary ions. This methodology is useful to reduce the ion yield changes, i.e. the matrix effects, during the sputtering throughout different layers [4]. Preliminary analyses were performed in different analytical conditions to check the reliability of the results. Best depth resolution was obtained by using sample rotation combined with low primary beam energy, i.e. 500eV.

Ellipsometric spectra were measured in the spectral range 300nm to 1700nm at 50°, 60° and 70° degrees. The spectra were analyzed using the dielectric functions obtained from reference samples of the same compositions ($\Gamma$-values) and annealed in the same conditions as the samples of this study. In the following we give the real part of the refractive indices at 633 nm , which reflects to some extent the excess-Si content in the reference samples: $\Gamma_3=2.46$, $\Gamma_{3N}=2.55$, $\Gamma_8=1.87$, $\Gamma_{8N}=1.87$, $\Gamma_{10}=1.81$, $\Gamma_{10N}=1.80$, $\Gamma_{15}=1.68$, $\Gamma_{20}=1.63$. This approach allows to reduce considerably the number of variables during the fitting of the ellipsometric spectra. The goodness of the fit was below 0.7 for all the samples (Table 2).

Morphology analyses of SRON layers on sample W14 were performed by AFM, with a NT-MDT Unisolver Scanning Probe Microscope. The layers can be removed in a controlled manner by SIMS sputtering until the chosen depth, i.e. the middle of each selected layer, has been reached. The surface was scanned in semi-contact mode, with a silicon tip radius less than 10nm (~10N/m, ~155kHz). W14 was then dipped in HF 8% solution for 10s; the aim of the additional etching is a further exposal of the nano-crystals. Morphology analyses after SIMS sputtering and after sputtering plus etching are compared.

3. Results and Discussion

Silicon depth profiles obtained by SIMS were quantified by using an approximate method, based on a fitting procedure between the lowest Si concentration (Si in stoichiometric SiO$_2$) and the highest Si
concentration (Si in Si bulk) [2]. Example of the result obtained on sample W14 is reported in figure 1. Depth scale was established from reference sample SiO2. Single layer thicknesses differ from the nominal values, as expected because of SIMS sputtering proceeds faster in Si matrix than in SiO2. Depth corrections are anyway difficult to be applied, because of heterogeneous matrices. Silicon atomic concentrations obtained by SIMS are reported in table 1. SIMS results depend on analytical conditions, mainly on the primary beam impact energy. Matrix effects and RSF variations throughout the layers are definitely unavoidable in SIMS analyses. Therefore the reported Si contents were calculated as mean values between the concentrations obtained at 3keV and 500eV.

The total layer thickness and the thickness of the single stacks obtained from analysis of the VASE spectra are given in table 2. The total thickness of the samples is very close to the ones obtained from SIMS. The thickness of the single layer differs from SIMS analysis. In same cases if the difference in the dielectric functions (refractive indices) is low, layers might even vanish in the VASE modeling (e.g. sample W8). The SIMS depth profiles show that in some cases, due to diffusion of Si at high temperatures among the single layers, the Si-depth profile is not well represented by a 3 or 4 layer model.

AFM images obtained on Γ20 and Γ3N sputtered layers are compared in figure 2 (a) and 2 (b). The parameter considered to compare the layers surface is their roughness root mean square Sq. The morphology of the layers seems nearly the same but in Γ3N layer the structures appear laterally connected. The silicon aggregation shapes seem not well separated and in particular they could be not spherical but form elongated and connected structures, as proposed by Müller [5]. Possible mutual interferences of the structured layers have to be pointed out, because of their shallowness. In fact the bumps periodicity estimated for silicon nano-crystals in the buried layers (about 30nm) exceeds the nominal layers thickness. Moreover SIMS sputtering starts on uneven Γ20 surface and follows its morphology, and similarly it follows the buried layers morphology, even if the sputtering process tends to smooth the surface. The smoothing effect during sputtering is well confirmed by reduced roughness Sq=0.33nm in the silicon substrate, compared to 0.57nm in the above Γ8N layer. Bumps in the silicon substrate are still present, but they are artefacts probably originated by SIMS analyses with sample rotation and they can be assimilated to smoothed traces of the above sputtered layers (figure 2 (c)). No bumps are visible on flat silicon wafer (figure 2 (d)) where Sq=0.1nm. The additional etching process in HF solution (8% for 10s) is selective for SiO2 and increases Sq in the SRON layers, less affecting Sq in the silicon substrate (table 1).

**Figure 1.** SIMS depth profiles on sample W14, obtained at 500eV Cs+ with rotating stage. Si is quantified by an approximate fitting method.

**Figure 2.** AFM images 500nm x 500nm on Γ20 (a), Γ3N (b), Silicon sub (c), on flat silicon wafer (d).
Table 1. Silicon atomic concentration and roughness in SRON layers, calculated by SIMS and AFM analyses. *data obtained on sample W14.

| matrix  | Si-content [at/cm³] | Roughness Sq [nm] sputtered layer* | Roughness Sq [nm] after etching* |
|---------|---------------------|------------------------------------|---------------------------------|
| Si sub. | 5.06x10²²           | 0.33                               | 0.46                            |
| Γ3N     | 4.0x10²²            | 0.53                               | 0.95                            |
| Γ8N     | 3.7x10²²            | 0.57                               | 1.1                             |
| Γ10     | 3.5x10²²            | --                                 | --                              |
| Γ15     | 3.3x10²²            | 0.48                               | 0.87                            |
| Γ20     | 2.8x10²²            | 0.47                               | 0.53                            |
| SiO₂    | 2.65x10²²           | --                                 | --                              |

Table 2. Multilayer structures of the samples with nominal layer thickness(1) and the layer thickness obtained from SIMS(2) and VASE(3) measurements. Γ =N₂O/SiH₄, N= 40 sccm of NH₃.

| sample  | Total thickness | 4th layer | 3rd layer | 2nd layer | 1st layer |
|---------|-----------------|-----------|-----------|-----------|-----------|
| W2      | 50 nm(1)        | Γ3 15nm   | 13 nm     | 15nm 23.2nm | 11nm 6.2nm |
|         | 39nm(2) 37.3nm(3) |          | 15 nm     | 20nm 15nm | 15nm 2nm  |
| W8      | 46 nm 45.3nm    | --        | 22 nm     | 32.9nm    | 11 nm 12.3nm |
| W14     | 49 nm 50.0nm    | Γ20 15nm  | 11 nm     | 15 nm 20.4nm | 17nm 13.8nm |
| W20     | 50 nm           | Γ3 15nm   | 11 nm     | 15nm 15nm | 15nm 10.1nm |
| W22     | 42 nm 39.2nm    | Γ15 15nm  | 11 nm     | 6.8nm 15nm | 15nm 26.2nm |
| SiO₂    | --              | --        | --        | SiO₂ 53nm |

Conclusions.
SIMS, VASE and AFM are pointed out as fruitfully combined analytical techniques which can provide physic-chemical and morphological characterization of SRON multilayer.

The fitting method applied on silicon depth profiles obtained by SIMS is confirmed as an approximate method but useful to reduce the spreading of the raw data. We find an excellent agreement for the total sample thickness for both SIMS and VASE analysis. The correspondence of the thickness of each single layer in the stacks obtained by the 2 different methods is sometimes bad. The origin is inter-diffusion of excess Si between the sub-layers resulting in a Si-concentration depth profile which might differ considerable from the ones assumed in VASE modeling.

SIMS sputtering combined with a chemical etching was used to finely tune the layer position where AFM analysis has to be performed. A chemical etching alone shall not be able to precisely target a depth and stop within a particular layer, if multilayer with a gradient in the silicon content is present, as occurs in SRON stack.

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