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Photoemission studies of very thin (<10 nm) silicon oxynitride (SiO_xN_y) layers formed by PECVD

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Abstract

The “ITRS Roadmap” suggests the necessity of working out the processing methods allowing formation of ultrathin dielectric layers with higher values of the dielectric permittivity than for silicon dioxide. The silicon oxynitride layers (SiO_xN_y) seem to be the most natural compromise. But still none of high temperature methods used for its formation can be seriously considered as final solution for future ULSI-CMOS ICs production due to the inevitable formation of nitride monolayers just at the silicon–insulator interface. The main scope of this investigation is to check if this is true.

The oxynitride layers were produced by PECVD method. The process has already been optimised in order to allow repeatable and reliable formation of ultrathin layers (<10 nm). These layers were investigated by photoelectron spectroscopy (PES) using variable excitation energy. This results in a variable escape depth of the photo electrons and thus the depth structure of the sample can be concluded. Due to the combination of chemical information and depth information this method is a unique tool for investigating the hidden nitride layers. In this work, we present a comparing study of oxynitride layers with different oxygen-to-nitrogen ratios and different post-deposition annealing temperatures investigated by the above described method. It will be shown that the main difference between certain preparation conditions is the SiO_{2-} and the nitride-content and that nitride and oxynitride is distributed nearly homogeneously.

Keywords: Semiconductors; Thin films; Vapour deposition; Photoelectron spectroscopies; Synchrotron radiation

1. Introduction

Oxynitrides are in the focus of materials research for the past years with the aim to replace the conventional SiO_2 for gate dielectrics. The main reason therefore is the larger dielectric constant ε of oxynitrides. In fact ε increases from a value of 3.9 for SiO_2 (SiO_2N_0) to 7.8 for Si_3N_4 ($SiO_0N_{1.33}$) almost linear with the nitrogen content in the oxynitride [1]. But also the diffusion suppressing properties of oxynitrides are of interest. Especially the suppression of the boron and phosphor diffusion [2] is advantageous as boron and phosphor are important dopants. But also the diffusion of atomic hydrogen H^0 is suppressed by oxynitrides [3].

Therefore, it is clear that the understanding of the formation process of oxynitrides grown by various methods (thermal oxidation and oxinitridation of Si by NO, N_2O and NH_3/chemical deposition like CVD or atomic layer deposition (ALD)/physical deposition like N-implantation or magnetron sputtering) is well investigated and is summarised in many review articles [4,5]. A main aspect of all these investigations always was the depth structure of the oxynitride films. Having the purpose of thin gate dielectrics in mind it is clear that the oxynitride layer have to be very thin, in the range of some nm. These ultrathin layers are already difficult to analyse due to the limited depth resolution of the mainly used depth profiling technique secondary ion mass spectroscopy (SIMS) because of ion mixing effects. To overcome this problem the ion scattering techniques medium ion energy scattering (MEIS) has been developed especially to investigate ultrathin layers [6]. But both methods deliver only information about the elemental distribution of, e.g. N, O, or Si within the layer, but no information about the chemical bonding of these elements. This information can be derived from photoelectron spectroscopy (PES). Due to its extreme surface sensitivity (the photoelectron inelastic mean

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free path λ (IMFP) is in the range of 1–3 nm) PES is limited to layers of a thickness less than 10 nm; just the thickness of ultrathin layers. Furthermore the IMFP can be varied by the kinetic energy of the photoelectrons and hence by the excitation energy used for PES. As PES always gives a sum signal from all layers within the analysed area the variation of the depth sensitivity of the PES can open up the possibility to derive a depth structure of the sample. To do this is the aim of this work utilising a synchrotron as a variable X-ray source.

2. Experimental

The ultrathin oxynitride layers were grown on Si wafers by a plasma-enhanced CVD process (PECVD). The PECVD process runs in a RF-plasma (13.56 MHz) in a planar (parallel plate) reactor. Two types of oxynitride layer were grown using different gases for the PECVD process: Layers with a low oxygen content are produced in NH_3:SiH_4 plasma, while layers with a high oxygen content are produced in N_2O:NH_3:SiH_4 plasma. A schematic view of the used PECVD set-up is given in Fig. 1.

As usually in PECVD processes, the process temperature is very low, i.e. <400 °C. This gives room for higher temperature annealing in N_2 ambient that followed the formation process in case of some of the samples. The annealing process is included in order to test the layers for high temperature stability—in fact they simulate high temperature annealing which is indispensable in typical CMOS processes (mainly—source and drain implantation activation). All prepared layer types investigated in this papers are shown in Table 1.

The PECVD preparation and post-formation treatment of the layers was done at the Institute for Microelectronics and Optoelectronics (IMIO) in Warsaw. For the measurements the samples were transferred to the synchrotron BESSY-II in Berlin-Adlershof/Germany. There samples of about 8 mm × 8 mm were first cleaned in an ultrasonic bath in isopropanol and then introduced into the vacuum system followed by a heating to about 300 °C to allow the adsorbed hydrocarbons to desorbe. By that cleaning process the carbon contamination could be decreased to approximately 1/10 of a monolayer or less as evident from survey spectra taken at 1000 eV.

The PES measurements were performed at the undulator beamline U49/2-PGM-2 supplying photons in the energy range of 80 eV–1500 eV with a resolution above 7000 ($E/\Delta E$). Charge compensation was not needed due to the thin oxide layer. The used spectrometer was a EA125 electron analyser made by Omicron NanoTechnology GmbH with a resolution of about 200 meV.

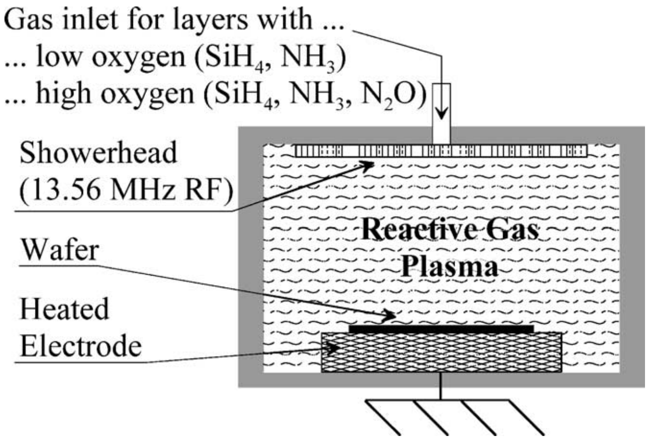

Fig. 1. Schematic view of the used PECVD reactor. By the use of SiH_4 and NH_3 oxynitride layers with low oxygen content were grown. Adding N_2O to the gas flux oxygen-rich layers could be grown.

3. Results

Following the idea of varying the depth information by varying the excitation energy the Si2p, N1s, and O1s core-level emissions were measured at different excitation energies respectively different IMFP λ of the photoelectrons (see Table 2).

To interpret the information about the chemical bonding conditions in the layer the measured spectra were analysed by a line decomposition. The single emission lines were assigned to a certain chemical compound due to their unique binding energy. An example for every core-level is shown in the following Fig. 2. It should be noted that the shown sample (high-oxygen content/600 °C anneal) was chosen exemplary to demonstrate all found emission line and its corresponding energetic position. Not on all samples were found all emission lines. Furthermore, the existence of some emission lines (e.g. the nitride line in the N1s spectrum in Fig. 2) is not compelling evident from only one spectra of a certain sample but is evident from the set of spectra (taken at dif-

Table 1
PECVD preparations and post-formation treatments investigated in this paper

PECVD preparation	Post-formation preparation		
Low oxygen content (SiH_4:NH_3)	None (as-prepared)	600 °C anneal	800 °C anneal
High oxygen content (SiH_4:NH_3:N_2O)	None (as-prepared)	600 °C anneal	800 °C anneal

Table 2
For PES used photon energies with their respective IMFP λ

Core-level (approximately binding energy) (eV)	Excitation energy, where the core-levels were measured				
	150 eV	450 eV	600 eV	750 eV	1000 eV
Si2p (100)	8.0[a]	13.8[a]	17.6[a]	21.2[a]	27.0[a]
N1s (400)		8.0[a]	9.9[a]	13.8[a]	20.0[a]
O1s (530)			7.5[a]	10.5[a]	16.8[a]

The IMFP were calculated by Tanuma et al. [7] and validated for Si/SiO_2 by Yamamoto et al. [8].

[a] Value for λ given in Angstrom units.

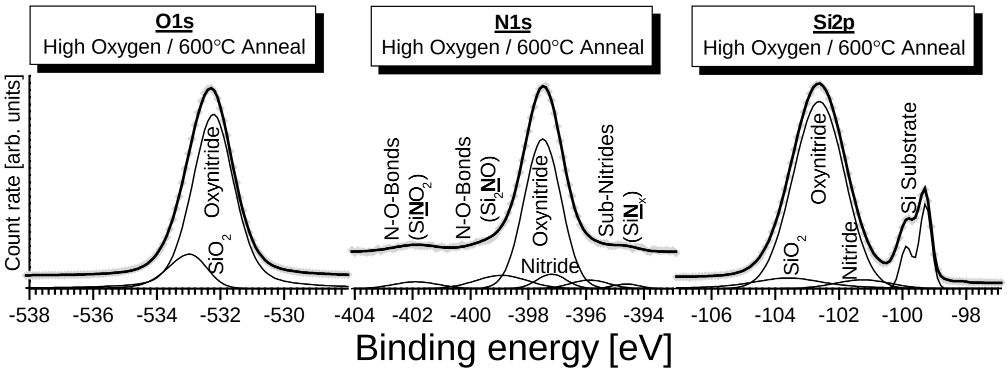

Fig. 2. Line decomposition for the O1s, N1s, and Si2p core-level emission taken at $h\nu = 1000$ eV on the high-oxygen content sample annealed to 600 °C. This sample was taken exemplary to demonstrate all found emission lines with its respective chemical compounds.

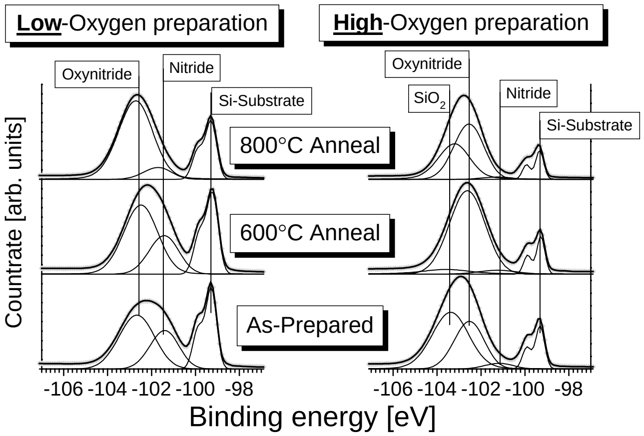

Fig. 3. Comparison of the Si2p spectra of all samples taken at $h\nu = 1000$ eV. The measured data (●) and the line decomposition (thick black lines) are shown. The single emission (thin black lines) are labelled with its belonging chemical compound.

ferent excitation energies) from these samples and from the other samples. So the necessity of e.g. the SiO_2-emission lines in the O1s and Si2p spectra or the nitride-emission lines in the N1s and Si2p spectra is evident. This can be seen in Fig. 3 when comparing the samples.

The line decomposition in Fig. 2 show only the results for one sample. On the other samples not all of these emission could be found. Emissions from SiO_2 are only present on the high-oxygen content samples whereas nitride emission are present at all samples but much stronger on the low-oxygen content sample. Oxynitride on the other hand is the dominating species on all samples. This can be seen already in the spectra shown in Fig. 3. Remarkable here is the large nitride content of the low-oxygen samples and the decrease of this nitride emission upon annealing (left hand side of Fig. 3). At the high-oxygen samples the SiO_2-emission line appears (right hand side of Fig. 3). Even here traces of nitride can be found. Like in the low-oxygen preparation the content of nitride and slightly the content of SiO_2 is decreasing.

Summarising these result an overview of the found chemical compounds is given in the Table 3.

4. Discussion

4.1. Comparison of the samples

From Fig. 3 and from the summary in Table 3 it can be concluded that oxynitride layers of the low-oxygen samples consist of approximately 60% oxynitride SiO_xN_y and 40% nitride Si_3N_4 (atomic ratio). Upon annealing the nitride will be oxidised and the nitride emission vanishes with increasing annealing temperature. Even on the high-oxygen samples the same behaviour can be found. There is much less nitride detectable but this vanishes too with increasing annealing temperature like on the low-oxygen samples. This can be seen in the ratios of the nitride/oxynitride emissions which are plotted versus the sample preparation in Fig. 4.

Table 3
Overview of the found chemical compounds in the different preparations. "✓" means the compound was found in an amount comparable to other compounds

Preparation	Low-oxygen content			High-oxygen content		
Post-formation treatment	As-prepared	600°C	800°C	As-prepared	600°C	800°C
SiO_2	...	...	...	✓	Minor	✓
Oxynitride	✓	✓	Dominating	✓	Dominating	✓
Nitride	✓	✓	Minor	Minor	Minor	Minor

"Dominating" indicates the dominating compound whereas "minor" indicates less prominent but detectable emissions. If "..." appears the compound was not detectable.

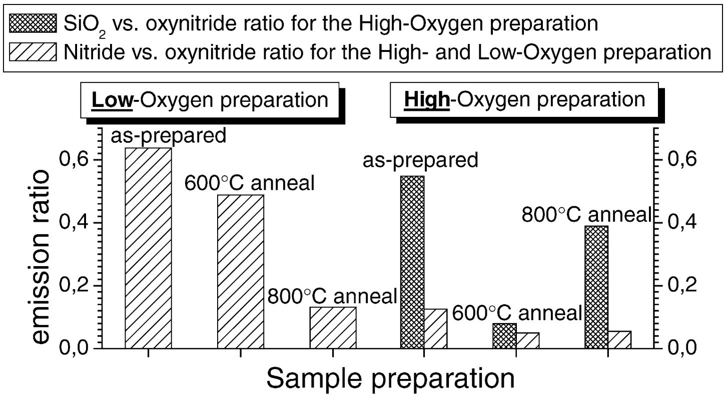

Fig. 4. Ratios of the SiO_2/oxynitride and the nitride/oxynitride emissions taken from the line decomposition in Fig. 3.

The vanishing of the SiO_2 emission with increasing annealing temperature is much less evident from the data. Like it can be seen in Fig. 4 there is a minimum SiO_2 content for the 600 °C annealed sample. It is not yet clear whether this is typical for samples annealed at low temperatures. Therefore, further experiments with intermediate anneal temperatures have to be performed.

4.2. Layer thickness calculation

The first step of the evaluation of the depth information is the calculation of the layer thickness. This thickness can be calculated from the intensity ratio of the oxidic ($I_{\mathrm{oxydic\,Si}}$) divided by the substrate ($I_{\mathrm{Si\,substrate}}$) emission obtained from the line decomposition of the Si2p spectra. Therefore, the following formula can be derived [9,10]:

$$d = \lambda_{\mathrm{SiO_2}}(E_{\mathrm{kin}}) \ln \left[\frac{I_{\mathrm{oxydic\,Si}}}{I_{\mathrm{Si\,substrate}}} \frac{I_0^{\mathrm{Si\,substrate}}}{I_0^{\mathrm{oxydic\,Si}}} \frac{\lambda_{\mathrm{Si}}(E_{\mathrm{kin}})}{\lambda_{\mathrm{SiO_2}}(E_{\mathrm{kin}})} + 1 \right] \tag{1}$$

Here $I_{\mathrm{oxydic\,Si}}$ and $I_{\mathrm{Si\,substrate}}$ are the measured intensities of the Si substrate and the oxidised Si (SiO_2, oxynitride, and nitride). Furthermore $I_0^{\mathrm{Si\,substrate}}/I_0^{\mathrm{oxydic\,Si}}$ is representing the intensity ration of infinite thick Si substrate versus infinite thick oxide what is influenced by atomic ratios and X-ray excitation cross-sections. This ratio was determined on Si/SiO_2. Applying formula (1) it is possible to calculate the layer thickness from every Si2p spectra taken at different excitation energies on a certain sample. As all calculated layer thickness on one sample should be the same, the standard deviation σ can be taken as a statistical error. The results including σ as an error bar are summarised in Fig. 5.

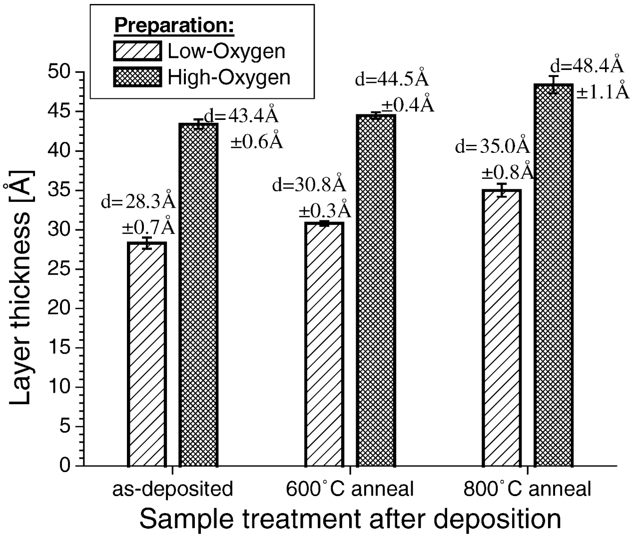

Fig. 5. Layer thickness calculated for every preparation including the standard deviation σ as a statistical error.

From Fig. 5 it can be seen that the layers grown with high oxygen content (in a $N_2O:NH_3:SiH_4$ plasma) have an about 50% larger thickness in general. This is understandable because SiO_2 growths faster then oxynitrides [4] and so a higher oxygen content in the growth ambient increases the growth rate. Furthermore, it can be seen from Fig. 5 that the layer thickness increases with the post-formation annealing temperature. And here it is evident that the low-oxygen content samples show a faster increase in layer thickness then the high-oxygen content samples. This is in agreement with the findings for the change in the chemical constitution of the layers where a much larger change in the nitride/oxynitride ration were observed for the low-oxygen layers. So the oxidation of the nitride seem to be one possible reason for the change in layer thickness. The needed oxygen therefore might come from “excess” oxygen within the layer (SiO_2– reduction, in case of the high-oxygen samples) or from the external environment while the annealing process.

4.3. Depth information evaluation

Depth information is contained in the PES spectra due to the exponential attenuation of the photoelectrons with increasing depth. By changing the attenuation length λ one can test the depth structure of the sample: If a chemical compound A is underneath a different chemical compound B the PES emission lines belonging to each chemical compound

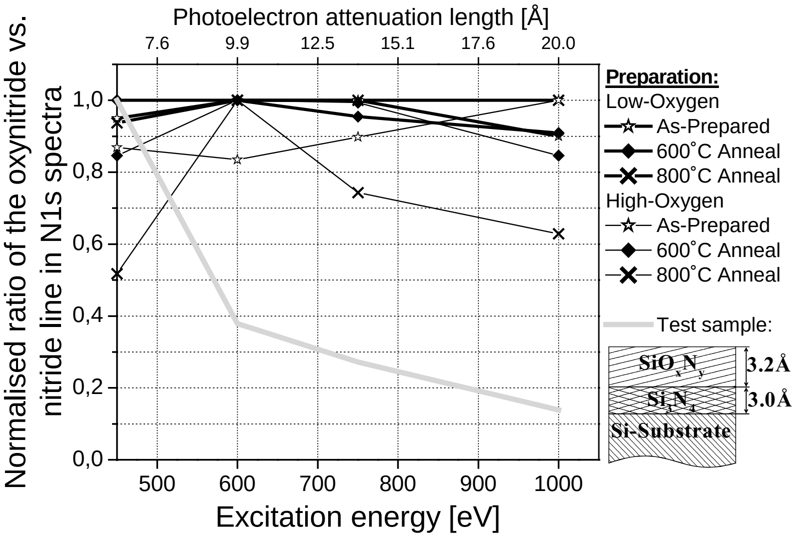

Fig. 6. Intensity ratio of the oxynitride/nitride emission from the N1s spectra of all samples investigated in this paper. The same intensity ratio for a test sample consisting of a layered structure of a Si_3N_4 layer between the Si substrate and the covering oxynitride layer is plotted for comparison.

A and B would show a relative shift in their intensities. In other words, the ratio of its intensities will change with the attenuation length in a certain (monotonic) way (see thick grey line in Fig. 6).

To check this for the PECVD oxynitride layers the intensity ratio of oxynitride to nitride ([oxynitride]/[nitride]) was plotted versus the excitation energy, respectively the attenuation length λ (see Fig. 6). Together with the PECVD samples the intensity ratios of a test sample prepared by a treatment of Si(1 1 1) in 1×10^{-4} mbar N_2O at 940 °C for 25 min are shown. Within that treatment conditions a layer-like structure of the test sample is grown. This was investigated with the same method of depth profiling using PES with variable excitation energy [9]. Compared to this layer-like test sample (see inset on the lower right of Fig. 6 for the depth structure of that test sample) there is no evidence for a layered structure in the data of these PECVD samples. In fact the low-oxygen samples show an almost stable intensity ratio. From this it can be concluded that the nitride and the oxynitride at least within the low-oxygen layers is distributed nearly homogeneous (mixed nitride and oxynitride). The intensity ratio of the high-oxygen layer shows a somewhat more complicate behaviour what indicates a non-homogeneous distribution of the nitride within the oxynitride. A detailed investigation of that distribution was not yet possible but the distribution can be investigated by simulation of the intensity ratio. But here one has to take into account that the low amount of nitride emission next to the large oxynitride emission (see middle in Fig. 2) results in a large error in the line decomposition. But never the less no such monotone behaviour of the oxynitride/nitride emission ratio like on the test sample (thick grey line in Fig. 6) was observed even for the high-oxygen samples. So it can be concluded that no layer-like distribution (e.g. Si_3N_4 layer next to the Si-oxynitride interface) is present even in the high-oxygen PECVD samples.

5. Summary

The PECVD oxynitride layers investigated here show a distinct chemical composition, whereas the low-oxygen layers consist of nitride and oxynitride the high-oxygen layers consist of a more or less amount of SiO_2 and traces of nitride, but the dominating chemical compound is oxynitride. With the post-formation annealing the layer thickness increases for all preparations and the nitride vanishes, what means it will be oxidised. This oxidation process, especially for the low-oxygen content samples, is understandable, because the depth analysis show that the nitride and the oxynitride is distributed nearly homogeneous and so nitride can be transformed into oxynitride because of the oxygen-rich neighbourhood of the nitride when thermal energy is supplied by the annealing process.

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