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Sputter deposition of undoped and doped SiO_2 films for temperature compensated SAW components

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***Abstract*—Reactive magnetron sputter deposition is shown to be a suitable method for depositing Fluorine doped silica films for temperature compensated SAW devices.**

Keywords—TC-SAW, SiOF, magnetron sputtering, reactive magnetron sputtering

I. Introduction

Silica (SiO_2) has the unique property of increasing stiffness with temperature. This makes it suitable for compensating the temperature drift of frequency in SAW components based on Lithiumniobat (LN) or Lithiumtantalat (LT) wafers. SiO_2 films with 1…2µm thickness on top of the interdigital transducer are typically used for this purpose. To reduce insert losses due to the SiO_2 film, mechanical properties of the film should be closed to fused silica. Therefore sputtering has established as dominant technology for the deposition of the SiO_2 films for temperature compensated (TC-) SAW, as it leads to films with very good mechanical properties within the temperature limitations of the typical SAW devices.

Recent publications showed that doping of the silica films with Fluorine leads to an even stronger stiffness increase with temperature [1]. Such films will be denoted as SiOF throughout the paper. SiOF films have the potential of achieving temperature compensation at reduced film thickness. This makes it feasible to reduce insertion losses and to improve temperature compensation when using SiOF rather than SiO_2 films [2].

Most of the work on SiOF films has been done up to now using PECVD deposition techniques [1, 2, 3]. PECVD processes typically require an elevated substrate temperature that may exceed the typical temperature limitations of SAW devices in the range of 250…300°C. Consequently sputter deposition is an attractive candidate to deposit SiOF films with good mechanical properties while observing the substrate temperature limit of SAW devices.

Up to now there are only few publications on sputter deposition of SiOF films [e.g. 4], probably mainly due to the fact that using fluorine containing gases requires special measures regarding personal and equipment safety that are not implemented at a standard sputter tool.

A detailed investigation on the sputter deposition of SiO_2 and SiOF films onto Si and LN substrates by reactive sputtering of Si targets in a mixture of the gases Ar, O_2 and NF_3 is presented in this paper. Compositional analysis, infrared spectroscopy (FTIR), measurement of refractive index and Young's modulus of the films are reported in dependence on process parameters like sputtering power, pulse mode, gas flows, substrate temperature, substrate bias and pressure. Furthermore, stability of the films upon annealing is investigated.

II. Experimental

A. Deposition set up

Depositions were done in the cluster-like sputter tool scia Magna 200. Reactive pulse magnetron sputtering with the Double Ring Magnetron DRM 400 sputter source developed by Fraunhofer FEP [5] was applied. This type of magnetron combines two concentric discharge targets to deposit uniform films on substrates with a diameter of up to 200 mm. Fig. 1 shows a schematic of the deposition set up. Depositions were done in either unipolar or bipolar pulse mode. Sputtering power was between 1 and 4kW at outer target and 0.2 and 1 kW at inner target of the DRM. The background of the different pulse modes, especially the significantly higher plasma density and thermal substrate load in bipolar mode has been reported elsewhere [6]. Total gas pressure was set to typically 0.3mbar by upstream control of Argon gas at approximately 40 sccm. The reactive gases Oxygen and Nitrogen trifluoride (NF_3) were used. Oxygen gas flow was adjusted to stabilize the process in the transition mode of the discharge. Typical values of O_2 and NF_3 flows were 20sccm and 1,8sccm respectively.

All depositions were done with rf substrate bias of typically 100W. In some experiments He backside cooling was used. The volume between the Si or LN wafer and a water cooled substrate stage was filled with Helium gas at 10mbar. Maximum substrate temperature during coating was measured using temperature labels attached to the substrates.

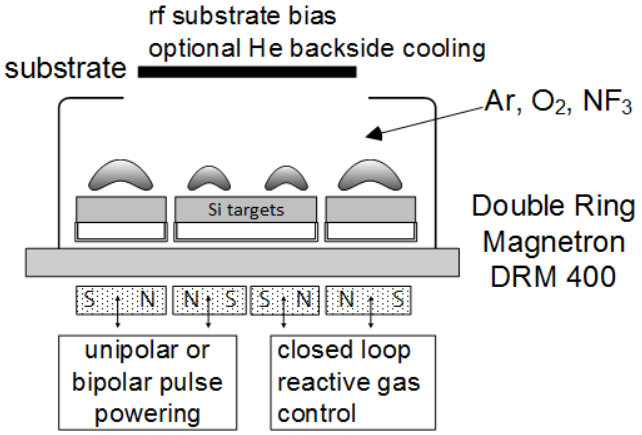

Fig. 1. Schematic of the deposition setup

B. *Film characterization*

Film thickness was measured at a Profiler Tencor P15-LS. Youngs modulus was measured using nanoindentation at the Nano Indenter XP of MTS. Refractive index was calculated from measurements at the spectroscopic ellipsometer SE 850 of Sentech. Density was derived from X-ray reflection (XRR) spectra. Film composition was determined by the EDX module of the SEM SU8000 (Hitachi).

C. *FTIR Analysiss*

Major element of film characterization was the FTIR spectroscopy. FTIR spectra were taken in transmittance on silicon substrates using a PerkinElmer Spectrum 2000, followed by a baseline correction. The FTIR spectra (Fig. 2) exhibit the typical absorbance bands of SiOF films (ω3 of Si-O at 815cm^{-1}, Si-F at 937cm^{-1}, ω4 of Si-O around 1070cm^{-1}, and the Phonon-phonon (P-P) peak of SiO_2 at around 1150cm^{-1}).

Two different ways of spectra analysis were tested. First, a deconvolution was performed (Fig. 2). In this case it was not possible to obtain satisfying agreement between measured and deconvoluted spectra, when only the mentioned peaks were considered. Especially the position of the ω4 Si-O peak seemed to be rather arbitrary in the deconvolution. However especially this peak position both in the Swope publication [3] and in our own experiments turned out to be the major parameter for describing the incorporation of Fluorine into SiO_2.

Hence in the further course of experiments another approach of FTIR spectra analysis was taken. SiOF thickness was kept in the narrow range of 1000±100nm to reduce inaccuracies caused by the fact, that intensity of the P-P peak depends significantly stronger on film thickness then the other intensities. Intensity of FTIR was normalized by film thickness. This yielded spectra of similar intensity and appearance that could be well compared, especially with respect to ω4 Si-O peak position, (see for example Fig. 3 and 5).

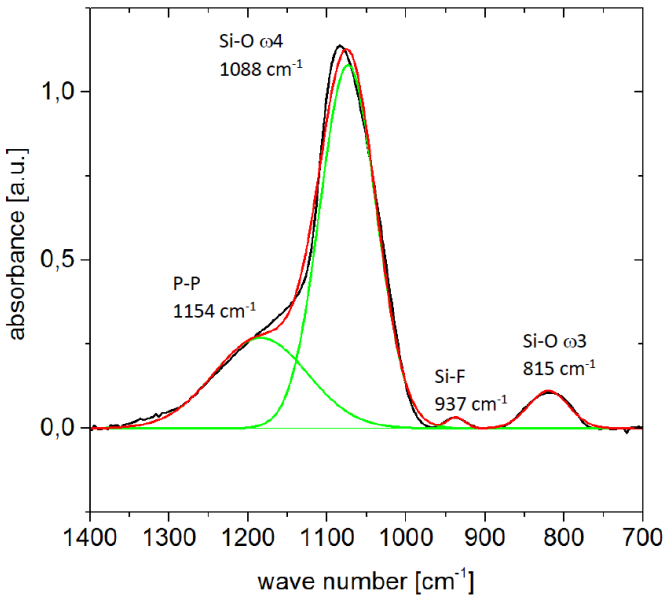

Fig. 2. Typical FTIR spectrum of SiOF film with deconvolution: Black original measurement data (after background correction), Green: deconvoluted peaks, Red: superposition of deconvoluted peaks

III. RESULTS

First SiOF depositions were performed in unipolar pulse mode (SiOF (uni)). Fig. 3 shows the measured FTIR spectra in dependence of NF_3 flow. It shows the expected formation of the Si-F peak and the shift of the ω4 Si-O peak. Further increase of NF_3 flow above 2sccm did not result in a significant further shift of ω4 peak position and was not considered in further experiments.

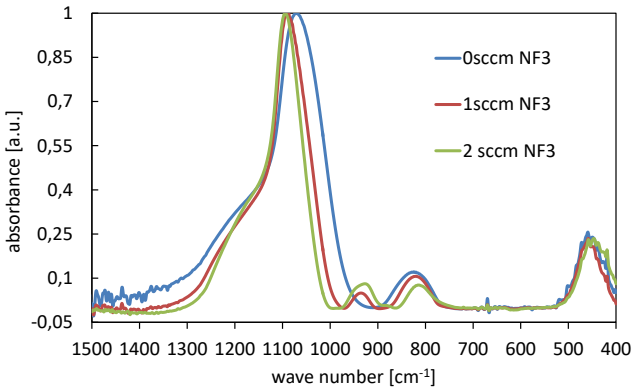

Fig. 3. FTIR spectra of SiO_2 and SiOF films deposited with various NF_3 flows in unipolar pulse mode

In bipolar pulse mode the NF_3 incorporation was investigated similarly (SiOF (bi)). Here the optimum Fluorine incorporation was found at 1,8sccm NF_3.

For all samples a percentage of Si-F bonds was calculated from the shift of ω4 Si-O peak compared to pure SiO_2 according to the dependency reported by Swope [3]. The stability of the films was investigated by annealing experiments. FTIR spectra were taken and atomic F concentration was measured using EDX before and after annealing at 350° (air, 1h).

Table I presents the results of these investigations. It shows first, that the percentage of Si-F bonds is considerably lower than the F-atomic content measured by EDX. This indicates, that only a minor part of F atoms is actively bound in the SiO_2 matrix. In bipolar mode this part is higher than in unipolar mode. By thermal annealing the samples deposited in unipolar mode show both a decrease in the ω4 Si-O peak position and in the EDX F-atomic content. On the other hand samples deposited in bipolar mode show only a slight decrease in the EDX F-atomic content and are stable in the FTIR spectra.

The more detailed investigation of the ω4 Si-O peak position on the annealing temperature is shown in Fig. 4. Absolute numbers differ from Table 1 because another set of samples was used. Whereas in bipolar mode ω4 peak position is stable within measurement accuracy, in unipolar mode there is first an increase in the wave number of peak position followed by a decrease at higher temperatures.

These results are interpreted under consideration of the significant differences in energetic substrate bombardment between unipolar and bipolar pulse mode [6]. The strong energetic substrate bombardment in combination with the resulting higher substrate temperature in bipolar pulse mode result in the formation of more stable films. In these films only part of the not actively bound Fluorine leaves the film, whereas the percentage of Si-F bonds remains constant. On the contrary the moderate energetic substrate bombardment in unipolar pulse mode yields less stable films that change both with respect to percentage of Si-F bonds and to F-content. Depending on the initial ω4 Si-O peak position the wave number of the ω4 peak either first increases and later decreases, as displayed in Fig. 4, or decreases from the beginning. After annealing at 400°C the properties of SiOF films deposited in unipolar and bipolar mode become similar.

TABLE I. COMPARISON OF SiO_2 (UNI) , SIOF (UNI) SIOF (BI) FILMS

	SiO_2 (uni)	SiOF (uni)	SiOF (bi)
Wafer temperature	175°C	175°C	260°C
ω4 peak position before anneal	1070 cm^{-1}	1091 cm^{-1}	1084 cm^{-1}
Percentage Si-F bonds [3]	0%	3.5%	1.7%
ω4 after anneal		1099 cm^{-1}	1084cm^{-1}
n @ 550 nm before anneal	1,48	1.43	1.44
n @ 550 nm after anneal		1.41	1.44
EDX atomic F-content	0%	15.6%	6%
EDX after anneal		8%	5.5%

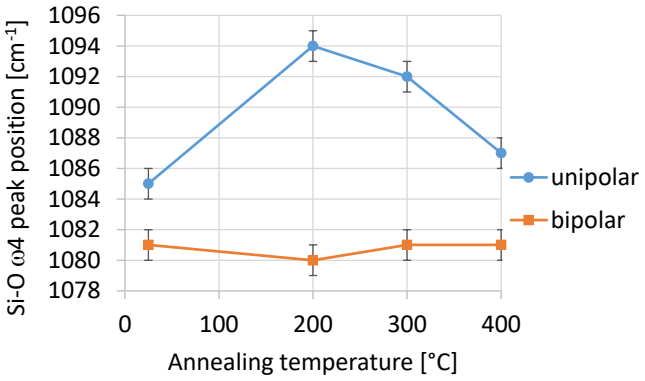

Fig. 4. Position of the ω4 Si-O peak after annealing at various temperatures

Because of the significantly better stability of the films deposited in bipolar pulse mode, only this pulse mode was used in further investigations. Two parameters were changed that significantly influence substrate temperature, the sputtering power (outer target: 4kW and 1kW) and the He backside cooling (cold=with He cooling, hot=without cooling). Results are shown in Table II. Temperatures above 260°C could not be measured with temperature labels at the final film thickness, but are estimated from measurements at lower film thicknesses, where the 260°C were not yet reached. In Fig. 5 the corresponding FTIR spectra are shown.

TABLE II. PROPERTIES OF SIOF FILMS DEPOSITED IN BIPOLAR PULSE MODE AT TWO DIFFERENT SPUTTERING POWERS (1KW AND 4KW) AND WITH [COLD] OR WITHOUT [HOT] HE BACKSIDE COOLING

	1 kW cold	**4 kW cold**	**1 kW hot**	**4 kW hot**
Wafer temperature	60°C	140°C	approx. 270°C	approx. 340°C
Deposition rate	0.6nm/s	2.1nm/s	0.4nm/s	1.2nm/s
FTIR Si-O ω4	1086 cm^{-1}	1088 cm^{-1}	1084 cm^{-1}	1084 cm^{-1}
Percentage Si-F	2 %	2,3%	1,7%	1,7%
EDX atomic F-content	10%	12%	5%	3%
Percentage active Fluorine	20%	19%	34%	57%
Refractive index (630nm)	1.43	1.42	1.45	1.45
Youngs Modulus	49 GPa	43 GPa	70 GPa	73 GPa
Density (XRR)	2.25 g/cm^{-3}	2.26 g/cm^{-3}	2.27 g/cm^{-3}	2.28 g/cm^{-3}

The following conclusions can be drawn:

- Beside pulse mode, the substrate temperature turns out to be a decisive parameter for the properties of SiOF films. ω4 peak position, atomic F-content, Young's modulus,

refractive index and density are strongly influenced by the substrate temperature.

- A percentage of active Fluorine incorporation was defined as ratio of percentage of Si-F bonds to EDX atomic F-content. This percentage increases with increasing substrate temperature. Samples can be sorted into two groups, one deposited "hot" with significantly higher percentage of active F. These groups can also be identified by features of the FTIR spectra. The "hot" group has lower FWHM of the Si-F peak and approaches the base line between Si-F and ω4 peak, whereas the "cold" group does not reach the base line. This may be an indication of the formation of a Si-F_2 peak consisting of superimposed Gaussian peaks at 900, 928 and 984 cm^{-1} [7]. It is assumed, that the percentage of active fluorine incorporation is also an important parameter for prospective application in SAW components.
- Films deposited in bipolar pulse mode at lower substrate temperature ("cold") are similar to the films deposited in unipolar pulse mode. However despite the lower substrate temperature during coating they exhibit a better stability. This clearly shows the importance of energetic substrate bombardment independent from the substrate temperature effect.

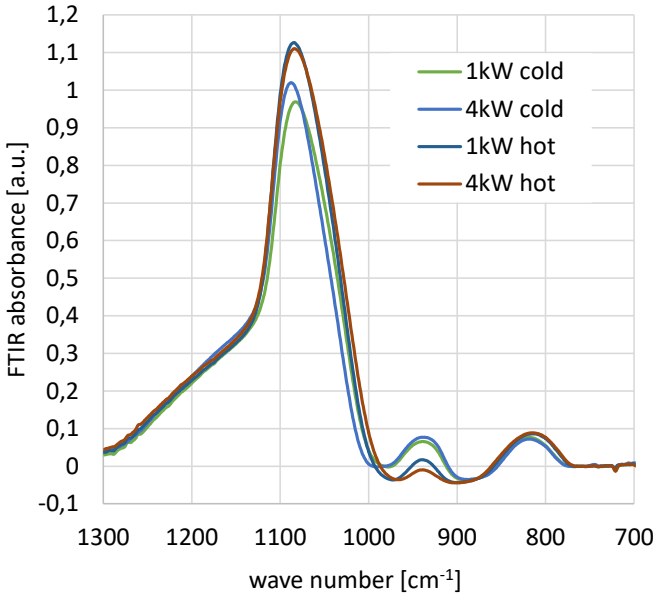

Fig. 5. FTIR spectra of SiOF films deposited in bipolar pulse mode (see Table II)

IV. Summary

It was shown, that properties of sputter deposited SiOF films especially depend on pulse mode, substrate temperature during deposition and on annealing conditions. The higher the temperature of either deposition or annealing the better the stability of the film.

Sputter deposition seems to be feasible of obtaining suitable SiOF films within the typical temperature limitations of SAW devices between 250 and 300°C. The high plasma density and strong substrate bombardment of bipolar pulse mode significantly improve the stability of the film. Best films are obtained in bipolar pulse mode at substrate temperature at the acceptable maximum.

FTIR analysis proved to be a useful tool for the evaluation of the SiOF film quality. ω4 Si-O peak position is a quantitative measure of Si-F bonds, FWHM of Si-F peak and the presumed formation of a Si-F_2 peak are qualitative measures for the ratio of active fluorine incorporation into the films.

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