

Self-regulating gas dosage for reactive RF sputtering of composition spread Hf oxy-nitride combinatorial layers

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Abstract

We aimed to prepare single sample concept composition-spread metal oxy-nitride layers by reactive radiofrequency sputtering for a highly efficient characterization of their optical properties in a wide range of O/N ratios. Affinity of metals requires oxygen proportion, in the Ar-O-N plasma, be set orders of magnitude lower compared to nitrogen. The required low partial pressure range of oxygen was covered by a new concept self-regulating gas inlet assembly based on a peristaltic pump delivering gas from a finite volume vial. We proved the suitability of our combinatorial method by both energy dispersive spectrometry mapping and ellipsometry of the correlated refractive indices along a 3-component composition-spread HfON sample.

Introduction

Thin layers of metal-oxy-nitrides (MeON) are widely used (Me denotes e.g. Al, Ti, Hf, Si) for wavelength selective coatings of optical elements, smart windows and laser diodes [x]. Their advantageous feature is the tunable refractive index by the proportion of the oxide and nitride components. Our aim was the synthesis of a single, concentration spread combinatorial sample in order to reveal the optical properties of various radiofrequency (RF)-sputtered metal-oxy-nitride layers in a wide range of O/N ratios. Recently „one sample concept” micro-combinatory has been developed [xi] for comprehensive characterization of two components “metal” (Me) films including Mn-Al [xii], Mg-Al [xiii] and Si-Ge [xiv, xv]. The deposition of gradient “Me-Me” samples is performed, through a moving slot, by means of DC magnetron sputtering from two targets of severally controlled power. We made further developments, currently to adapt micro-combinatory to reactive RF sputtering: a composition-spread layer is deposited from a single Me target by RF sputtering, meanwhile the ratio of the reactive components (O and N) in the plasma gas is varied. As we want to cover a composition range of the deposited film from Me-oxide to nitride the oxygen partial pressure has to be varied well below $1 \cdot 10^{-4}$ mbar. Unfortunately, the common gas dispensers cannot provide both the required low flow rates and fine control of partial pressures. We propose a self-regulating assembly for gas inlet: Oxygen is introduced to the chamber by a peristaltic pump emptying a finite volume reservoir. As oxygen is pumped out, the pressure in the reservoir gradually decreases. If gas is supplied at a constant volume rate from a reservoir of decreasing pressure, the mass transport rate will, as well, decrease. Therefore, the partial pressure of the oxygen gradually decreases towards base pressure of the sputtering chamber, while that of argon and nitrogen is kept constant by using conventional flow meters. A continuous depletion of the Ar-O-N reactive gas mixture in oxygen, during deposition, enables the deposition of composition spread oxy-nitride combinatorial samples.

Materials and methods

According to our experiments an oxygen partial pressure change between $1 \cdot 10^{-4}$ and $1 \cdot 10^{-5}$ mbar is suitable to cover a composition range of the deposited layer between Hf-oxide and Hf-nitride. Therefore, a device is required to regulate oxygen injection in this pressure range. The setup of the proposed self-regulating gas inlet assembly is represented by the scheme in figure 1. (a) that shows the sputtering chamber with the attached peristaltic pump connected to the oxygen reservoir (vial).

Prior to reactive RF sputter deposition of combinatorial samples a dedicated experiment was carried out. For this test, our RF sputtering chamber (Leybold Z400) was used. The vial of 48 cm³ volume was filled

with 1 bar oxygen and the volume rate of the peristaltic pump was set to 1 cm³/min. As the sputtering chamber was evacuated, by a turbo molecular pump, to its base pressure of about 6·10⁻⁷ mbar the peristaltic pump was started and it began to deliver O₂ from the vial into the chamber. As oxygen appeared in the chamber, the pressure suddenly increased to 9·10⁻⁵ mbar followed by a continuous decay due to a decrease of the delivered gas from the gradually emptied vial. The pressure in the chamber was measured, as a function of time, until it decreased to 1·10⁻⁵ mbar and then the peristaltic pump was stopped. The elapsed time was 110 minutes. The variation of the pressure in the chamber as a function of pumping time is plotted with full circles, in the diagram of Figure 1 (b). An O₂ partial pressure range between 9·10⁻⁵ and 1·10⁻⁵ mbar covered by our gas inlet assembly is considered to be suitable to deposit the designed composition spread Me oxy-nitride samples.

Modelling the gas inlet assembly

In addition to the dedicated experiment peristaltic pumping from a finite volume vial can be modeled by repetitive application of the general gas equation. Let p_{N2} be the pressure of the vial in the nth minute:

$$p_{N2}=p_0(1-v/V)^n \quad (1)$$

where p₀ is the manifold pressure of the V-volume vial and v volume of the O₂ gas pumped out during one minute. The p_{O2} partial pressure change at 1sccm O₂ inlet into the vacuum system was determined by the dedicated measurement. It was found to be 0.9·10⁻⁴ mbar right after the start of the peristaltic pump, and with a sudden transient it dropped to 0.8·10⁻⁴ mbar which is considered the initial value. The final pressure of the system was chosen to be 10⁻⁶ mbar, hence p_{O2} can be estimated as follows:

$$p_{O2}=0.1+8(1-1/V)^n \quad (2)$$

(n is the elapsed time in minutes)

The pressure change as a function of time, modeled according to equation (2), is plotted with a solid line in Figure 1 (b). It starts at an initial value of 8·10⁻⁵ mbar and shows an asymptotic decrease towards 1·10⁻⁶ mbar. The elapsed time until it reached 1·10⁻⁵ mbar was about 105 minutes. The HfON composition spread layer was deposited onto a 25x10 mm² Ge wafer placed behind a shutter with a narrow (1 mm) slot that was swept along the substrate by a stepping motor. The scheme of substrate and shutter is shown in fig.1 a. at the lower part of the chamber. The stepping motor moved the slot by 25 μm per step. The control was performed by a microcontroller, which allowed the speed of shutter to be varied over a wide range. Sputtering was performed under 10 to 1 mixture of high purity nitrogen and argon at a plasma pressure of 2.5·10⁻² mbar. Subsequent to pre-sputtering the target for 10 minutes O₂ gas was introduced from the 48 cm³ vial with 1 bar initial pressure, by the operation of the peristaltic pump. Peristaltic pumping was maintained for 110 min at a volume rate of 1cm³/min (causing a steady decrease of O₂ partial pressure in the chamber from 9·10⁻⁵ to 1·10⁻⁵ mbar), meanwhile, Ar and N pressures were kept constant. The sweeping time of the slot above the substrate was set to be in sync with the duration of O₂ inlet.

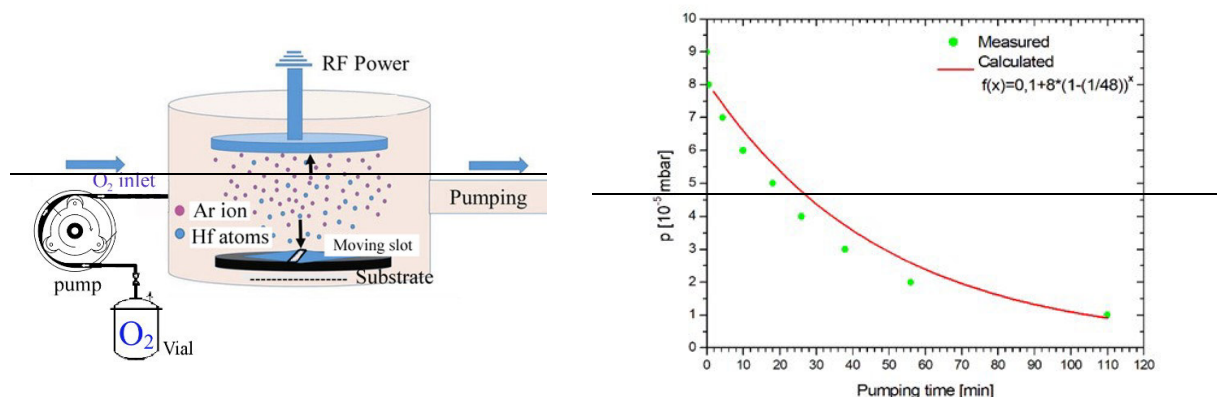


Figure 1. (a) Setup of the self-regulating gas inlet. (b) Variation of oxygen partial pressure in the sputtering chamber during an oxygen inlet experiment: the peristaltic pump was operated at a rate

of $1\text{ cm}^3/\text{min}$ emptying the 48 cm^3 vial of 1 bar initial pressure. Measured pressure decay during the experiment (●). Calculated pressure decay according to equation 2 (—).

Sputtering the Hf target in an Ar-O-N reactive gas mixture from which oxygen was gradually depleted resulted in a continuous drop of the O/N ratio in the deposited HfON. The deposit was laterally distributed along the substrate by the sweeping slot, so that a composition spread film was formed covering the range of transition from Hf-oxide to Hf-nitride.

The properties of the combinatorial Hf-oxy-nitride sample prepared as above were investigated by EDS and ellipsometry measurements. For to reveal the effects of the variation of oxygen inlet on the oxygen and nitrogen proportion of the layer the composition was determined along the sample by EDS in a FEI Scios scanning electron microscope using 3 keV probe with 13 nA current. The O/(O+N) ratio as a function of distance along the combinatorial layer is plotted in fig.2.

The optical properties of the combinatorial sample along the substrate were investigated by means of a spectroscopic ellipsometer with a rotating compensator configuration (Woollam-2000DI). The variation of refractive index revealed as a function of distance along the sample is plotted in fig.2. According to the dedicated test the assembly for variable oxygen gas inlet has worked properly.

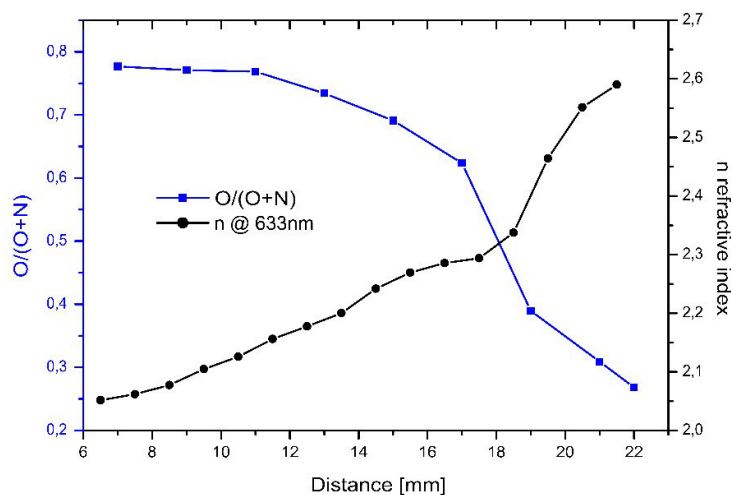


Figure 2. Variation of O/(O+N) and refractive index along the combinatorial Hf-O-N sample revealed by EDS (■), and n by ellipsometry at 632.8 nm wavelength (●), respectively.

The covered oxygen partial pressure range between $9 \cdot 10^{-5}$ and $1 \cdot 10^{-5}$ mbar revealed by both measurement and modelling was suitable to deposit a composition spread Me oxy-nitride sample. The correlations of composition of sputtering gas and that of deposited film, as well refractive index variation are revealed and presented in Fig.2. as a function of position along the combinatorial sample. The O/(O+N) ratio curve characteristic to the film composition, measured by EDS, depicted with full squares, shows monotonous decrease along the sample. It is in response to the gradual oxygen depletion of plasma gas during reactive sputtering. O/(O+N) values extending between 0.78 and 0.27 indicates that the combinatorial layer covers a wide composition range of HfON. The correlated refractive index values measured by ellipsometry and evaluated by the methods and parameters of [xvi, xvii] are depicted with full circles. It shows a monotonous transition of n -values between 2.05 and 2.6. Obviously, refractive index variation of the combinatorial sample covers about the entire composition range between stoichiometric HfO_2 [xviii, xix] and HfN [xx, xxi]. The results shown in fig.2 are illustrating that one sample concept combinatorial technique was successfully adapted to reactive RF sputter deposition and that the synthesized combinatorial sample is suitable to a comprehensive characterization of Me-oxy-nitrides in a wide composition range.

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