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## Optimization of silicon-rich silicon nitride films for electron multiplication in timed photon counters

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### Abstract

The excellent overall properties of silicon nitride, particularly its mechanical strength and resistance to many etchants, make it a widely used material for microsensors and microactuators. In this paper silicon-rich silicon nitride (SRN) films were investigated as material for ultra-thin transmission dynodes in electron multiplication. These dynodes are a fundamental element of ultrafast timed-photon counters (TiPC). The film properties were tuned to obtain SRN with higher conductivity so to suppress charging up effects, while maintaining or further reducing the low stress level required to fabricate the 20-50 nm thick dynodes. By optimizing low pressure chemical vapour deposition (LPCVD) process, SRN layers with very low compressive stress ( $\pm 10$  MPa) and very low resistivity ( $\pm 10^{10}$  Ohm·m) are obtained.

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Keywords: silicon rich silicon nitride; ultra-thin dynode; electron multiplication; secondary electron yield

### 1. Introduction - Timed photon counter

A Timed-photon counter (TiPC) is a novel detector for photons, electrons and energetic charged particles. The main advantages of a miniaturized TiPC over existing photodetectors are its reduced size, lack of noise and MEMS fabricated ultra-thin dynodes as a core innovation. Unlike traditional photomultiplier tubes, dynodes we produced are operating in a transmission mode, which allows significant reduction in size of TiPC [1].

Primary electrons that hit dynodes on the upper side will generate secondary electrons that come out from the bottom side of these ultra-thin windows. Vertical stacking of a few of such dynodes put at different potentials, results in an output signal that can be detected by a specifically designed pixel read-out chip. Each dynode contains dome-shaped protrusions with a pitch of 55  $\mu\text{m}$ . Such conical geometry is more rigid than flat membranes and

contributes to a better focusing of electrons away from non-active area of the read-out chip [1]. A schematic drawing of TiPC's configuration is shown in Fig. 1. The secondary electron yield (SEY) of silicon nitride, not well determined in present literature, will set the number of multiplication stages of the final device. With  $SEY = 4$  and  $N = 5$ , where  $N$  stands for number of dynodes, an average charge of 1000 electrons is collected by the pixels input pad, which is sufficient for detection.

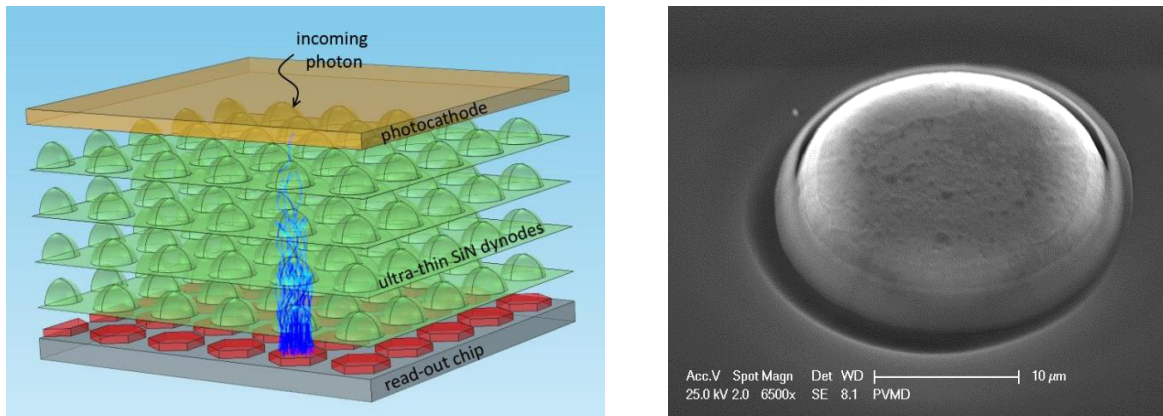


Fig. 1. Layout of TiPC (left): first dynode is at positive potential with respect to the photocathode. SEM image of a single dynode with diameter of 20 μm before final release of silicon nitride (right).

## 2. Experiment and results

It is of highest importance that the material of the dynodes in TiPC has low stress and high emission yield. For this purpose SRN was optimized to achieve low specific resistivity. Layers are deposited by low pressure chemical vapour deposition (LPCVD) process which is a widely applied method in the microsystem technology as it results in a conformal step coverage and a very good uniformity of thickness and composition. In this experiment depositions are performed in a hot-wall reactor which use dichlorosilane ( $SiH_2Cl_2$ , DCS) as a source of silicon and ammonia ( $NH_3$ ) as a source of nitrogen. Total gas flow was kept constant at 400 sccm while ammonia/DCS ratio ranged from 60/340 to 35/365. The main goal was to gain a lower resistivity and investigate possible changes in stress by varying gas flow ratio, i.e. by increasing silicon content in the film. Therefore, influence of other parameters such as temperature and gas pressure are not subject of this study (their values are set to 850°C and 150 mTorr, respectively). As a substrate we used standard 4-inch single side polished <100> Si wafers, doped with phosphorus ( $5 - 10 \Omega \text{ cm}$ ) and  $525 \pm 15 \mu\text{m}$  thick. Prior to deposition the wafers are cycled through a standard cleaning procedure, consisting of treatment in nitric acid (99% and 65%) with rinsing in de-ionized water and spin-drying.

### 2.1. Optical, mechanical and electrical properties of SRN films

The optical, electrical and mechanical properties of LPCVD silicon-rich silicon nitride (SRN) films with three different levels of silicon doping are studied. It is confirmed that the ratio of process gas flow has a strong effect on the film characteristics, as was shown by other authors [2, 3]. The dynodes used in TiPC need to be less than 50 nm thick, but for the material characterization 1 μm-thick layers were grown.

Thickness and optical properties of the SRN films are determined by ellipsometry. An overview of the deposition parameters together with the measured characteristics is given in Table 1. As expected, by increasing the DCS flow we obtained SRN with higher content of silicon and higher refractive index.

Table 1. Parameters in applied recipes and data on some properties of grown LPCVD SRN films.

Sample ID	NH <sub>3</sub> flow [sccm]	DCS flow [sccm]	Thickness [nm]	Stress [MPa]	Resistivity [Ohm m]	Si:N ratio [%]	Refr. index at 633 nm
1	60	340	1015	200	$1.4 \times 10^{13}$	45:55	2.20
2	40	360	1028	100	$0.8 \times 10^{11}$	49:51	2.34
3	35	365	999	-30	$2.0 \times 10^{10}$	50:50	2.40

Residual stress was calculated by using measurements of wafer curvature before and after SRN deposition with Tencor FLX 2908. Prior to measuring the curvature after deposition it was necessary to remove the film on the backside of wafer. This was done by reaction ion etching process under the following conditions: CH<sub>4</sub>/SF<sub>6</sub>/O<sub>2</sub> = 70 sccm / 10 sccm / 10 sccm , pressure = 50 mTorr, power = 60 W. An excess of DCS decreases residual stress of SRN and even converts it from tensile to compressive as measured for sample 3 (sign ‘-’ in front of stress value in Table 1. stands for compressive). This result is in agreement with other reports [4].

A new procedure for in situ measurements of the specific resistivity of SRN involving so called Micromegas was performed. The Micromegas detector is a modern 2D variant of a Geiger-Muller detector in which the output signal charge is proportional to the ionization charge in a gas-filled volume. In this in-situ method there is no need to apply a second contact electrode and accurate measurements of the total current, surface area and voltage drop are possible [5].

## 2.2. Secondary electron yield of SRN films

For investigation on the SEY of prepared samples a method that relies on photon-stimulated electron emission was developed. Samples were irradiated by low-energetic photons (150 – 420 eV). A change of the photon energy influences the depth of primary electrons excitation. The SEY is estimated by measuring the low energy tail of the XPS spectrum and comparing it to the rate of high energy electron emission. As a reference sample, a hydrogen terminated diamond is used, since its SEY is already reported [6]. The Si/N ratio was measured via energy dispersive x-ray spectroscopy in a scanning electron microscope. It was observed that sample 1 suffered from charging and loss of SEY and reliable results could be obtained for that type of SRN. On the other hand, samples 2 and 3 proved to be sufficiently conductive to sustain electron emission without charging.

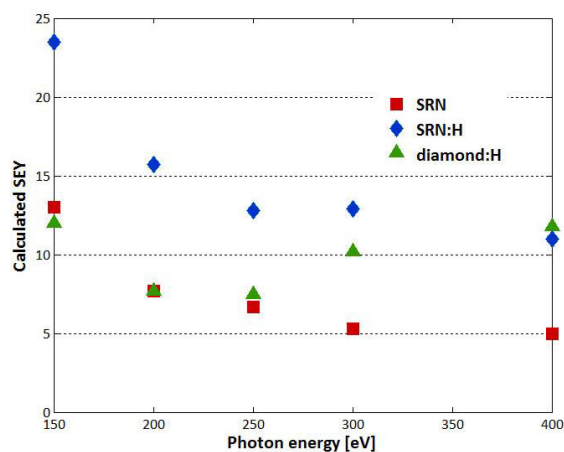


Fig. 2. Calculated SEY for SRN sample 3 (Table 1) before and after hydrogen termination and compared to hydrogen-terminated diamond at different photon energies [7].

The SEY can be tuned by altering electron affinity of a material. Usually this is achieved by surface terminations. In this experiment the effect of oxygen and hydrogen terminations is investigated/studied. For hydrogen termination, a plasma system was used where samples were heated to 500°C and exposed to RF plasma for an hour at approximately 50 mTorr. This method is modeled to resemble procedures commonly applied for diamond [6]. The calculated SEY for sample 3, hydrogen-terminated sample 3 and diamond terminated sample, using the same procedure, are plotted in Fig.2. Hydrogen termination indeed increases SEY of SRN in comparison with a non-treated SRN. Results for sample 2 are similar to sample 3 and therefore are not presented here.

### 3. Conclusions

By tuning the ratio of DCS and ammonia in LPCVD process we deposited three different SRN films. Apart from the good mechanical properties of these layers, it is shown that the layers with the two higher content of silicon had resistivity which is low enough to suppress charging effects in the proposed system for SEY measurements.. Hydrogen termination of such SRN (SRN:H) layers resulted in a significantly higher value of SEY. For this reason SRN:H would be a good choice for working material of ultra-thin dynodes in TiPC.

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