

SILICON NITRIDE THIN-FILMS BY RF SPUTTERING: APPLICATION ON SOLID STATE LITHIUM BATTERIES

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Abstract — Silicon nitride is the most common barrier material to protect microsystems from atmosphere, usually deposited through CVD techniques. In this paper our aim is to highlight the advantages brought by using PVD techniques, namely RF sputtering, to deposit silicon nitride thin-films. In particular, we intend to protect microsystems fabricated only by PVD techniques and avoid the necessity of a second CVD chamber to do the microsystem coating. The influence of gases (Ar/N₂) during deposition was correlated with film composition and with measured electrical and optical properties. Featuring electric resistivity of $9.51 \times 10^{11} \Omega \cdot \text{cm}$, a breakdown field of 1.67 MV/cm and refractive index between 1.92 and 1.84 (measured at 650 nm) silicon nitride deposited by RF sputtering is a good complementary layer of Li₃PO₄ or Ti for the protection of metallic lithium anode of solid state lithium batteries.

Keywords : Protective coating; RF sputtering; silicon nitride thin-films; solid state lithium batteries.

I - Introduction

Silicon nitride is mainly applied in microelectronics as an insulator and a chemical barrier for protective packaging of devices. As a passivation layer, it presents a higher diffusion barrier against water molecules and sodium ions, which is essential in microelectronics [1]. In addition, silicon nitride has high thermal stability, elevated hardness and good dielectric properties [2]. In optics, it provides great transparency in spectral range from 300 to 1200 nm. Therefore, it's possible to use it in biochemical and biomedical optical applications [3].

Typically, silicon nitride thin-films are fabricated by chemical vapor deposition at low gas pressure (LPCVD) and plasma-enhanced (PECVD) [4]. Nevertheless, RF sputtering depositions offer some advantages over previously mentioned techniques, such as absence of toxic gases (replaced by inert gases); lower deposition temperature (for bio and organic applications); versatility and simplicity to change the parameters of film growth [5]; and a lower stressful stoichiometry [6].

In the present article, we intend to use silicon nitride as a complementary protective coating on solid state lithium batteries only fabricated using PVD techniques. A battery is composed by two electrodes (cathode and anode) and one electrolyte between them, acting as an electrical insulator (figure 1). In lithium batteries, the anode is normally metallic lithium, which oxidizes very

quickly in contact with air and water. Thus, it is essential to achieve an effective protection for lithium anode.

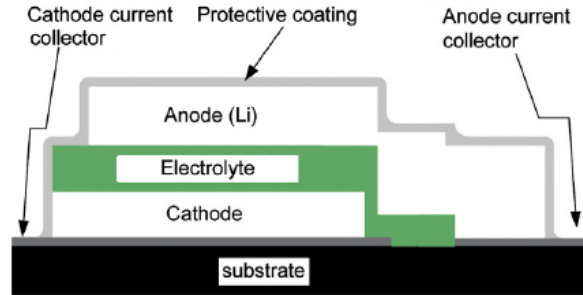


Figure 1: Schematic of a planar solid state lithium battery [7].

Different protection layers were already tested in our previous work [8]. Taking this as starting point, our purpose is to complement this first protective layer with silicon nitride fabricated by RF sputtering. Thereby, a complete lithium battery will be fabricated in series, resorting only to PVD techniques, avoiding the necessity of a glove box and a CVD chamber.

II - Experimental Details

The properties of silicon nitride thin-films were evaluated through Energy Dispersive X-ray Spectroscopy (EDS), dielectric charging, and optical transmittance.

To conduct these tests, aluminum contacts (thickness of 200 nm) were deposited by E-Beam technique on a glass substrate. The aluminum was patterned by photolithography and wet-etching. To measure the electric resistivity and breakdown field in Si_xN_y thin-films, aluminum was deposited and patterned on the top of Al + Si_xN_y film, to create a MIM (metal-insulator-metal) structure, as presented in figure 2.

In order to evaluate the influence of gases during sputtering, 5 different samples were prepared assuming a total flow of 20 sccm in the vacuum chamber (table 1). The nitrogen and argon had a high purity (99.9992 %). The distance from samples to target was 75 mm.

Table 1: Ratio of gases, deposition rate and temperature during deposition for different samples

Sample	Nitrogen [sccm]	Argon [sccm]	Deposition rate [Å/s]	Temperature [°C]
#01	20	0	0.7	79
#02	16	4	0.8	79
#03	13	7	0.8	80
#04	10	10	0.9	79
#05	7	13	1.0	76

The thin-films of Si_xN_y were deposited by RF sputtering (13.56 MHz) at a constant pressure of 6×10^{-3} mbar, applying 250 W of power. A 2" silicon wafer was used as sputtering target. This wafer has the following specifications: single side polished, [100] orientation, and 1 mm thickness.

The thickness and roughness of deposited films were measured in 4 points using a *Dektak 150 Surface* profilometer. The stylus had 12.5 μm of diameter and applied a force of 30 μN . The mean thickness of Si_xN_y films was 516 ± 58.7 nm, with a roughness of 1.64 nm. Regarding Al contacts, the structures had a width of 133 ± 2.5 μm , 231 ± 2.8 μm , and 529 ± 7.8 μm , presenting 2.08 nm of roughness.

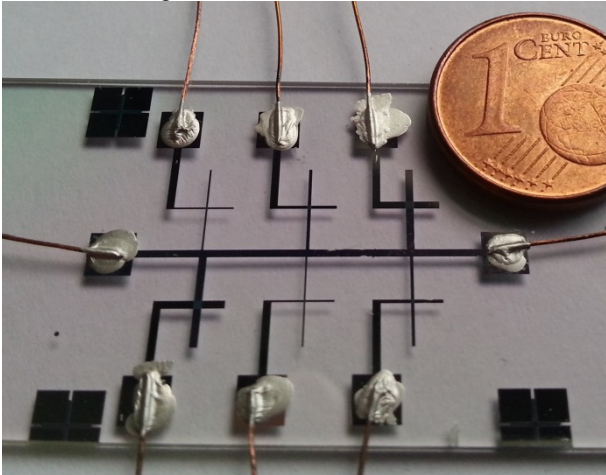


Figure 2: Si_xN_y thin-films between different Al patterns with copper wires connections fixed with silver glue.

III - Results and Discussion

A. Composition

The composition of films was analyzed through EDS (Energy-dispersive X-ray spectroscopy). For that purpose, Si_xN_y were also deposited in a sample of stainless steel and Kapton[®] polyimide (HN type, 50 μm thick). Despite the reduced percentage of nitrogen contained in Kapton[®] (around 7%), composition was similar in both substrates, as shown in figure 3. The horizontal axis represent the N_2 flow, divided by the total gas flow ($\text{N}_2 + \text{Ar}$), and the vertical axis the nitrogen or silicon content of the film. The Kapton[®] substrate tested will enable the future use of silicon nitride as protective coating on flexible microsystems, such as flexible lithium batteries.

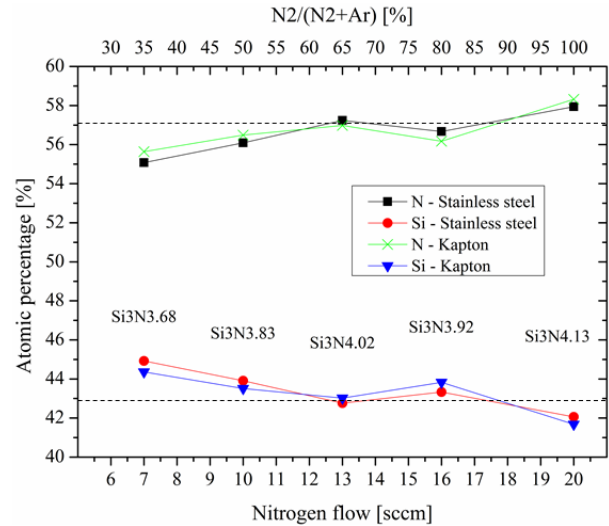


Figure 3: Atomic percentage of nitrogen and silicon from Si_3N_y films deposited on stainless steel and Kapton[®] substrates (dashed lines represent stoichiometric Si_3N_4).

As expected, more incorporation of nitrogen in the film is obtained with higher nitrogen flow during deposition.

B. Dielectric charging

The electric resistivity and breakdown field of Si_xN_y thin-films was measured with the structure of figure 2. All measurements were performed at room temperature, with picoammeter *Keithley 6487*, controlled by an own made *LabView* software. A DC voltage (alternating between positive and negative value in each measurement) was applied in two complementary ways, namely: i) 0-10 V with 0.2 V step; and ii) 0-500 V with 2 V step. The current measurement was taken after 600 milliseconds of voltage application. Electrical resistance was measured with 1 V applied to the film. Breakdown field was measured dividing the maximum applied voltage without disruption by film thickness.

Figure 4 and figure 5 display the electric resistivity and breakdown field for Si_xN_y thin-films deposited by PVD. Furthermore, it compares PVD results with our previous results of Si_xN_y thin-films deposited by hot-wire CVD at 100 $^\circ\text{C}$ and 250 $^\circ\text{C}$ [9], using silane (SiH_4) and ammonia (NH_3) highly diluted in hydrogen (H_2). Both resistivity values were calculated with 1 V applied. The horizontal axis represent the N_2 flow divided by the total gas flow ($\text{N}_2 + \text{Ar}$) in PVD and the NH_3 flow divided by SiH_4 flow in CVD. The vertical axis represent electrical resistivity (figure 4) and breakdown field (figure 5). Literature reported electric resistivity of 10^{16} $\Omega\cdot\text{cm}$ by CVD, and 10^{11} $\Omega\cdot\text{cm}$ by RF sputtering (similar to our samples) [10]. The latter is higher for increased nitrogen ratios.

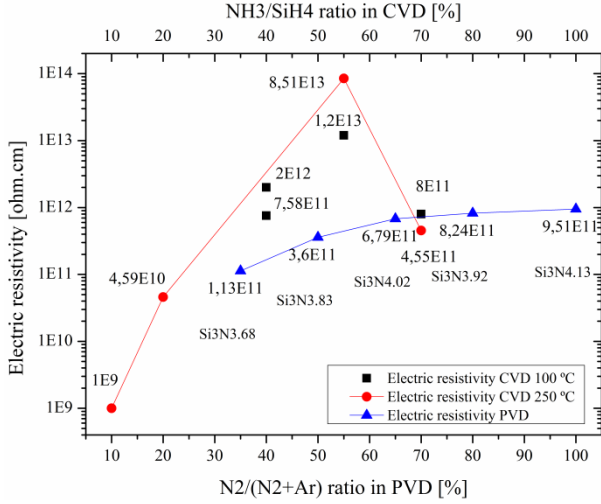


Figure 4: Electric resistivity as function of N_2 percentage (diluted in Ar) during PVD deposition and as function of NH_3/SiH_4 ratio (diluted in H_2) during CVD deposition.

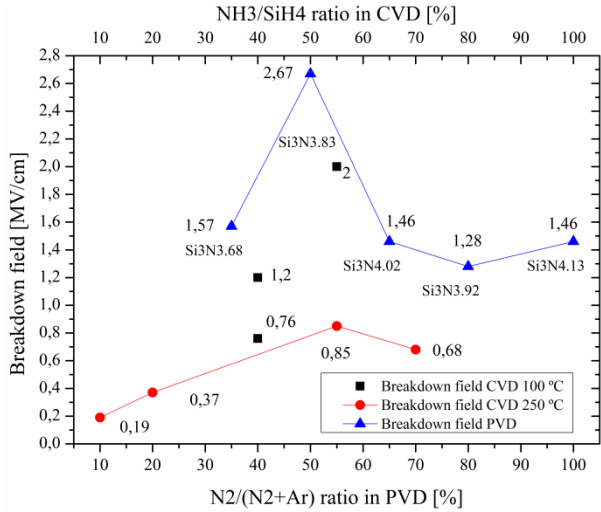


Figure 5: Breakdown field as function of N_2 percentage (diluted in Ar) during PVD deposition and as function of NH_3/SiH_4 ratio (diluted in H_2) during CVD deposition.

C. Optical transmittance

In order to complete the Si_xN_y thin-films characterization, optical transmittance measurements were performed. Film thickness and refractive index were calculated using the method proposed by Swanepoel [11]. Thus, a power of 200 W was applied in the lamp of the spectrophotometer (Oriel 66881). The monochromator (Corner Stone 130 1/8m) made scanning of the wavelength from 300 to 1000 nm and the correspondent light was applied on Hamamatsu Photodiode Model S1336-5BQ, controlled by LabView software. The step used in the wavelength was 1 nm and the mean of four readings was calculated for the current in photodiode.

The refractive index of the transparent substrate (s) was 1.52, considering a mean transmission of 91.8%. From the transmission spectrum of figure 6, and taking as starting point the extremes of the interference fringes T_M and T_m and their correspondents $T_{M'}$ and $T_{m'}$, the

refractive index can be calculated through equations (2) and (3), as demonstrated by Swanepoel [11].

$$N = 2s \frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2} \quad (2)$$

$$n = [N + (N^2 - s^2)^{1/2}]^{1/2} \quad (3)$$

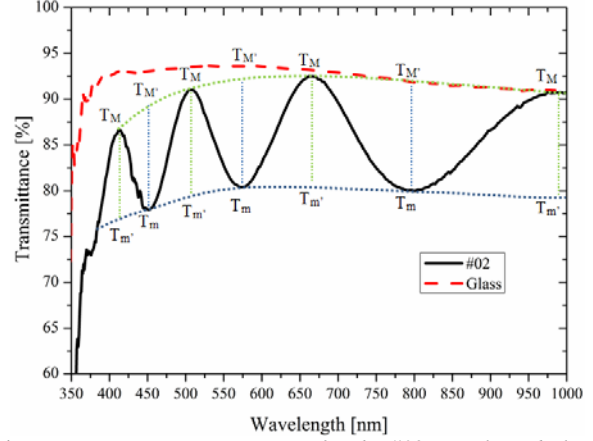


Figure 6: Transmission spectrum for the #02 sample and glass substrate as function of wavelength.

Considering two adjacent wavelength and refractive index, the thickness (d) is given by equation (4).

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \quad (4)$$

With the interference fringes equation (5) it's possible to determine (m), as stated by Swanepoel [11]. Thereafter, we recalculated a further accurate refractive index (n) and thickness (d) of the Si_xN_y thin-films using this simple straightforward formula from the transmission spectrum alone.

$$2nd = m\lambda \quad (5)$$

Mean thickness calculated was 518 nm, a very accurate result when compared with profilometer measurements (516 nm). The refractive index of the Si_xN_y thin-films by PVD ranged from 1.92 to 1.84, at 650 nm wavelength (figure 7).

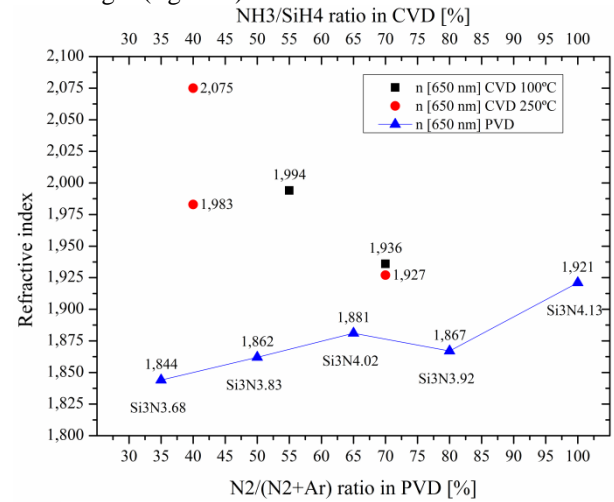


Figure 7: Refractive index (measured at 650 nm) as function of N_2 percentage (diluted in Ar) during PVD deposition and as function of NH_3/SiH_4 ratio (diluted in H_2) during CVD deposition.

These results were not corrected using the split width correction previous proposed [11].

Refractive index of stoichiometric amorphous Si_3N_4 was 2.05, which is higher than films obtained by PVD, and nearly the same value measured in CVD films.

D. Application on solid state lithium batteries

Lithium oxidization was individually evaluated with different protective layers [8]. On top of Al + Ti contacts (300 nm each one by E-Beam on glass substrate), lithium was deposited, followed by the protective layer. For the first 2 hours Li_3PO_4 was the best protection while, for longer periods titanium presented best performance (figure 8). On top of this protective layer, silicon nitride will be used as a barrier layer. Silicon nitride was also previously deposited directly on lithium. However, reactions occurred in lithium surface during the deposition of Si_3N_4 . Thus, an intermediate layer of Li_3PO_4 or Ti is proposed [8].

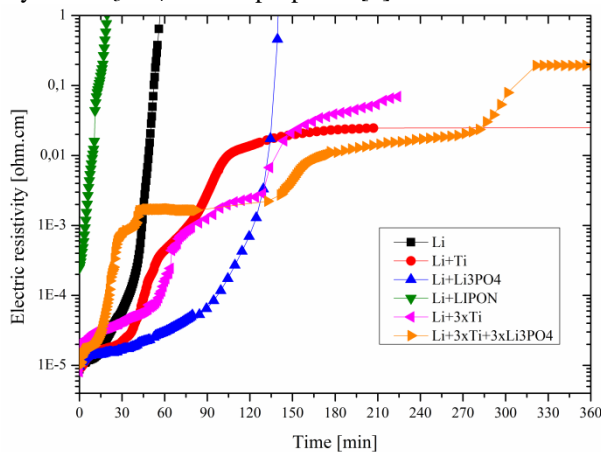


Figure 8: Resistivity of lithium for different protective layers when in contact with air [8].

IV - Conclusion

Silicon nitride is an effective protective layer for several applications. This study outlines how these applications can benefit from the advantages of RF sputtering depositions without compromising film properties. In this work, we reported an electric resistivity of $9.51 \times 10^{11} \Omega \cdot \text{cm}$ (similar to previous work on CVD [9]) and a mean breakdown field of 1.67 MV/cm. Refractive index between 1.92 and 1.84 (at 650 nm) were measured.

In future, silicon nitride will be characterized as barrier layer in lithium batteries. However, due to reaction of lithium during deposition of Si_3N_4 , an intermediate layer of Li_3PO_4 (for first 2 hours) or Ti (for longer periods) will be used. Therefore, silicon nitride may provide a wide range of applications as a complementary protective coating, including the metallic lithium anode of lithium batteries, without the necessity of a glove box and a second chamber with CVD.

Acknowledgments

This work was financial supported by FCT funds with the project PTDC/EEAELC/114713/2009, second author scholarship SFRH/BD/78217/2011 and strategic project from Algoritmi Centre FCOMP-01-0124-FEDER-022674.

References

- [1] W. H. P. Pernice, M. Li, D. F. G. Gallagher, and H. X. Tang, "Silicon nitride membrane photonics," *Journal of Optics A: Pure and Applied Optics*, vol. 11, no. 11, p. 114017, Nov. 2009.
- [2] H. Schmidt, W. Gruber, G. Borchardt, M. Bruns, M. Rudolphi, and H. Baumann, "Thermal stability and crystallization kinetics of sputtered amorphous Si_3N_4 films," *Thin Solid Films*, vol. 450, pp. 346–351, 2004.
- [3] G. Xu, P. Jin, M. Tazawa, and K. Yoshimura, "Optical investigation of silicon nitride thin films deposited by r.f. magnetron sputtering," *Thin Solid Films*, vol. 425, no. 1–2, pp. 196–202, Feb. 2003.
- [4] F. H. P. M. Habraken and A. E. T. Kuiper, "Silicon nitride and oxynitride films," *Materials Science and Engineering: R: Reports*, vol. 12, no. 3, pp. 123–175, Jul. 1994.
- [5] M. A. Signore, A. Sytchkova, D. Dimaiò, A. Cappello, and A. Rizzo, "Deposition of silicon nitride thin films by RF magnetron sputtering: a material and growth process study," *Optical Materials*, vol. 34, no. 4, pp. 632–638, Feb. 2012.
- [6] A. P. Mousinho, R. D. Mansano, L. S. Zambom, and A. Passaro, "Low temperature deposition of low stress silicon nitride by reactive magnetron sputtering," *Journal of Physics: Conference Series*, vol. 370, p. 012015, Jun. 2012.
- [7] J. F. Ribeiro, R. Sousa, J. P. Carmo, L. M. Gonçalves, M. F. Silva, M. M. Silva, and J. H. Correia, "Enhanced solid-state electrolytes made of lithium phosphorous oxynitride films," *Thin Solid Films*, vol. 522, pp. 85–89, Sep. 2012.
- [8] J. F. Ribeiro, R. Sousa, J. A. Sousa, B. M. Pereira, M. F. Silva, L. M. Gonçalves, M. M. Silva, and J. H. Correia, "Rechargeable lithium film batteries – encapsulation and protection," *Procedia Engineering*, vol. 47, pp. 676–679, Jan. 2012.
- [9] P. Alpuim, L. M. Gonçalves, E. S. Marins, T. M. R. Viseu, S. Ferdov, and J. E. Bourée, "Deposition of silicon nitride thin films by hot-wire CVD at 100 °C and 250 °C," *Thin Solid Films*, vol. 517, no. 12, pp. 3503–3506, Apr. 2009.
- [10] M. Vila, C. Prieto, and R. Ramírez, "Electrical behavior of silicon nitride sputtered thin films," *Thin Solid Films*, vol. 459, no. 1–2, pp. 195–199, Jul. 2004.
- [11] R. Swanepoel, "Determination of the thickness and optical constants of amorphous silicon," *Journal of Physics E: Scientific Instruments*, vol. 16, no. 27, 1983.