Study of Oxidized-Porous Silicon as Insulating Film for HI-PS Field Emission Devices

Débora A. C. Silva, Michel O. S. Dantas
Centro de Engenharia, Modelagem e Ciências Sociais
Universidade Federal do ABC
Santo André, São Paulo, Brazil
55 11 4996-8262
michel.dantas@ufabc.edu.br

Elisabete Galeazzo, Henrique E.M. Peres, Francisco J. Ramirez-Fernadez
Departamento de Engenharia de Sistemas Eletrônicos
Universidade de São Paulo
São Paulo, Brazil
55 11 3091-5310

ABSTRACT
This paper reports the study of Oxidized-Porous Silicon (Ox-PS) as insulating film for integrated Field Emission Devices (FE) fabricated by Hydrogen-Porous Silicon (HI-PS) technique. The PS thermal oxidation was conducted by varying process parameters such as temperature, time, and post-oxidation annealing. Morphological analysis by means of Fourier Transform-Infrared Spectrometry (FTIR) and optical microscopy indicated a fully oxidation of PS layers for all experimented process parameters. Metal-Oxide-Semiconductor (MOS) devices were fabricated to allow the electrical characterization of leakage current through Ox-PS from I-V curves. By applying the appropriated oxidation process parameters and post-oxidation annealing, a strong reduction of leakage current was characterized (from nA to pA) for the same bias level. This result indicates that Ox-PS obtained from suitable parameters is promising for use as insulating film in FE devices fabricated by HI-PS.

Keywords
Oxidized Porous Silicon (Ox-PS), Field Emission Device (FE), HI-PS (Hydrogen Implant – Porous Silicon)

1. INTRODUCTION
Field emission devices (FE – devices that allows the electron extraction by applying of a strong electrical field in microstructures with singular tip geometry aspect) has been widely studied due their excellent electric characteristics such as low power consumption, high current density, room temperature operation, among others [1-3]. They are promising for applications based on devices known as "cold cathodes": high-resolution optoelectronic systems, flat displays, x-ray sources, and gas sensing for example [4-8].

Several techniques and materials can be applied to obtain FE devices [5]; in special, silicon (Si) based FE are interesting due to the possibility of their integration with microelectronic circuit, which is promising for the development of miniaturized sensors. A technique named HI-PS (Hydrogen Implant – Porous Silicon) was proposed as a viable alternative to fabricate Si FE devices [9]. The advantages obtained with HI-PS include the use of compatible CMOS processes with low complexity to obtain the devices.

Despite the good results achieved with HI-PS technique, FE devices fabricated with integrated anode-cathode (which are basic structures of a FE device) in the same substrate present operational problems related to the poor electrical insulation between these two structures. PSG [10] and TiO_2 [11], among other dielectrics, can be used as insulator layers in FE devices, but silicon dioxide (SiO_2) is the traditional material used with this purpose since is totally compatible with CMOS processing [12-14]. All these insulators are generally obtained from CVD processes due to their relative large thicknesses (between 500 nm and 1 μm, depending on the size of the cathodes).

In the original HI-PS developed process, the electrical insulation is promoted by a SiO_2 film growth from dry thermal oxidation conducted with process times about 10 hours [9]. Even the relative large thickness of the SiO_2 film obtained in this process (about 1 μm) is not enough to guarantee an effective electrical insulation between anode-cathode structures, causing malfunction of the HI-PS FE device. Another relevant aspect is that the dimensions of cathode geometries obtained by HI-PS (with height about 10 μm) demand insulating films with the same order of magnitude, which difficult or even prevents the use of these traditional materials and processes.

One proposed alternative to solve this problem could be the use of Oxidized Porous Silicon (Ox-PS) layers as insulator. The Ox-PS, due to its singular properties, is explored in several applications such humidity sensing based on nanotechnology, electrical insulation in microwave devices and integrated circuits based on SOI technology, among others [15-20].

The oxidation parameters applied to form Ox-PS are quite distinct when compared with the consolidated SiO_2 films: high thickness PS layers (about tens of micrometers) can be fully oxidized with relative short process times (about tens of minutes) and with temperatures lower than 1000º C. It is possible due to its large inner surface and high reactivity with oxidant species [18]. Another remarkable characteristic is the possibility to obtain dielectric constant K values closer to the SiO_2 (about 3.8) depending on the anodization parameters applied to obtain PS [15, 17]. Nevertheless, the most attractive aspect is that Ox-PS is obtained from Si substrates with PS layers, which are the basis of the HI-PS processing, thus, it could be incorporated in the FE fabrication process without introducing additional complexity or cost.

Based on the exposed, this work focuses on the study of Ox-PS for applications as insulating film layer between the anode and cathode structures in FE devices obtained by HI-PS, aiming to reduce the leakage current from the bulk to the anode, and promoting consequently an effective electron emission current from the cathodes.

2. EXPERIMENTAL PROCEDURE
As described before, Ox-PS is formed from oxidation of PS layers, which were obtained in this work by anodization of Si wafers as follows: first, BF_2^+ ions were implanted at the backside of p type Si wafers (<100>, ρ = 10-20 Ω.cm); second, they were annealed (parameters: T = 900º C, t = 30 minutes, N_2 environment) to promote ohmic contact (necessary to the

electrochemical process); third, anodization was conducted to form PS layers (parameters: T = 40º C, t ≅ 14 minutes, concentrated HF solution (49% wt)).

After anodization, the PS layers were thermally oxidized in dry O_2 environment by varying the oxidation conditions (A, B, C and D) as described in Table 1. A post-oxidation annealing (T = 750º C, t = 120 minutes, "Forming Gas" environment) was also experimented in some samples to verify the improvement of dielectric characteristics.

Optical microscopy and Fourier Transform-Infrared Spectrometry (FTIR) were used to evaluate the morphology. For the electrical characterization, an aluminum layer (300nm thick) was deposited and photolithographed over Ox-PS layers to obtain MOS devices, and the leakage current was analyzed from I-V curves measured with a HP4156 Semiconductor Parameter Analyzer.

Table 1. Oxidation Parameters

Oxidation Condition	Temperature (T = º C)	Time (t = minutes)	Post-oxidation annealing
A	800	20	_____
B	1000	20	_____
C	1000	60	_____
D	1000	60	T = 750º C t = 120 min. "Form. Gas"

3. RESULTS AND DISCUSSION

3.1 Morphological Analysis

Figure 1(a) shows optical microscopy images of the sample surfaces before and after oxidation of PS. All adopted temperatures and times were apparently enough to promote total oxidation of PS layers. No thickness variations of the layers were verified before (Figure 1(b)) and after oxidation (Figure 1(c)), but surface cracks were observed in samples oxidized in the temperature of 800º C (Figure 1(d)), preventing these samples to be electrically characterized. Small cracks were observed on samples oxidized in the temperature of 1000º C for 20 minutes, and they were completely avoided in the samples oxidized in the same temperature (T = 1000º C), but with oxidation time increased (60 minutes – Figure 1(e)). These results indicate that temperatures below 1000º C or fast oxidation times can introduce mechanical stress in the Ox-PS layers, promoting their crack.

FTIR spectrometry was used to verify if the oxidation parameters were effective to promote total oxidizing of the PS layers. Figure 2 shows the spectra obtained. The curve (a) of Figure 2 presents the typical as formed PS spectrum [21], where the presence of peaks related to silicon-hydrogen bonds is noted: $Si\text{-}H_3$ "bending" (628 cm^{-1}), $Si\text{-}H_2$ (2100-2108 cm^{-1}), $Si\text{-}H_2$ "wagging" (665 cm^{-1}) and $Si\text{-}H_2$ "scissors bending" (910-916 cm^{-1}) [22]. The presence of silicon-oxygen bonds (Si-O (1160 cm^{-1}), Si-O-Si "asymmetric stretching" (984 cm^{-1}) and Si-O-Si "stretching" (1070 cm^{-1})) occurs because the high reactivity of this material to environment exposure.

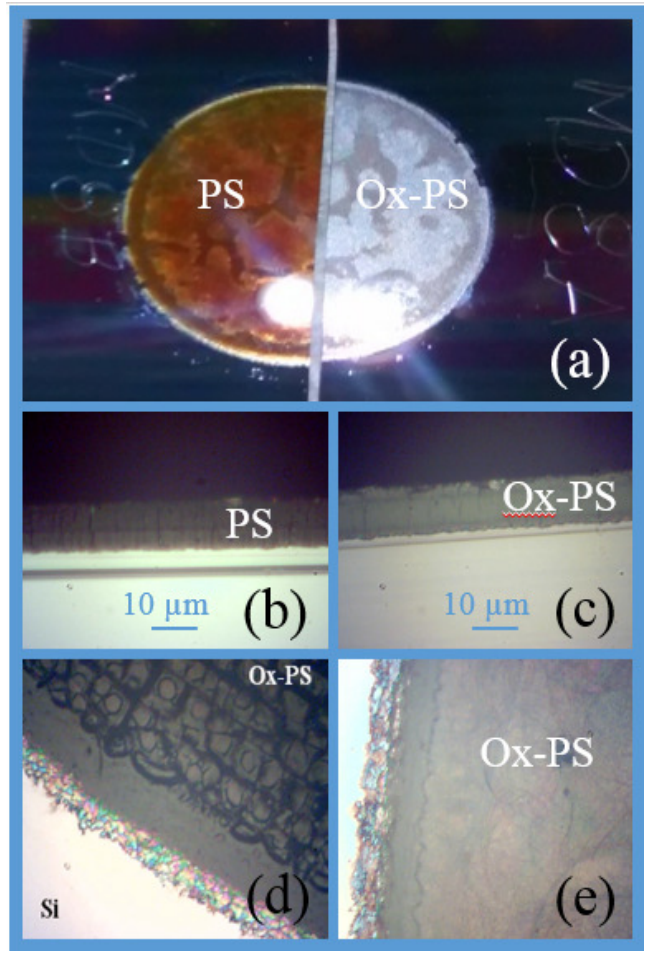

Figure 1. (a) Sample split showing PS (left) and Ox-PS (right) obtained with T = 1000º C and t = 20 minutes. (b) Cutaway view of PS layer and (c) Ox-PS layer (T = 1000º C and t = 20 minutes). (d) Cracks on sample oxidized with T = 800º C and t = 20 minutes. (e) Sample without cracks evidence, oxidized with T = 1000º C and t = 60 minutes.

The Ox-PS (Figure 2 (b-e) spectra) shows the complete elimination of silicon-hydrogen bonds, the increasing of silicon-oxygen bonds (Si-O (1160 cm^{-1}), Si-O-Si "asymmetric stretching" (984 cm^{-1}) and Si-O-Si "stretching" (1070 cm^{-1})), and the emergence of peaks related to "new" silicon-oxygen bonds: SiO_x (450 cm^{-1}), Si-O-Si (470 cm^{-1}) and Si-O-Si "symmetric stretching" (810 cm^{-1}) [22-24]. The wide "cut at the top" peaks noted between 984 cm^{-1} and 1210 cm^{-1} (related to silicon-oxygen bonds) indicate the saturation of IR detector due to the relative large thickness of Ox-PS layers (about 10 µm).

The Ox-PS spectrum of the sample oxidized with T = 800º C and t = 20 minutes (Figure 2, (b) spectrum) shows a little peak referent to carbon type bonds ($Si\text{-}CH_3$ (1640 cm^{-1})), probably due to the sample handling. In summary, the replacement of typical PS silicon-hydrogen type bonds for silicon-oxygen type bonds in all oxidized samples indicates that the parameters adopted were effective to promote total oxidation of PS layers.

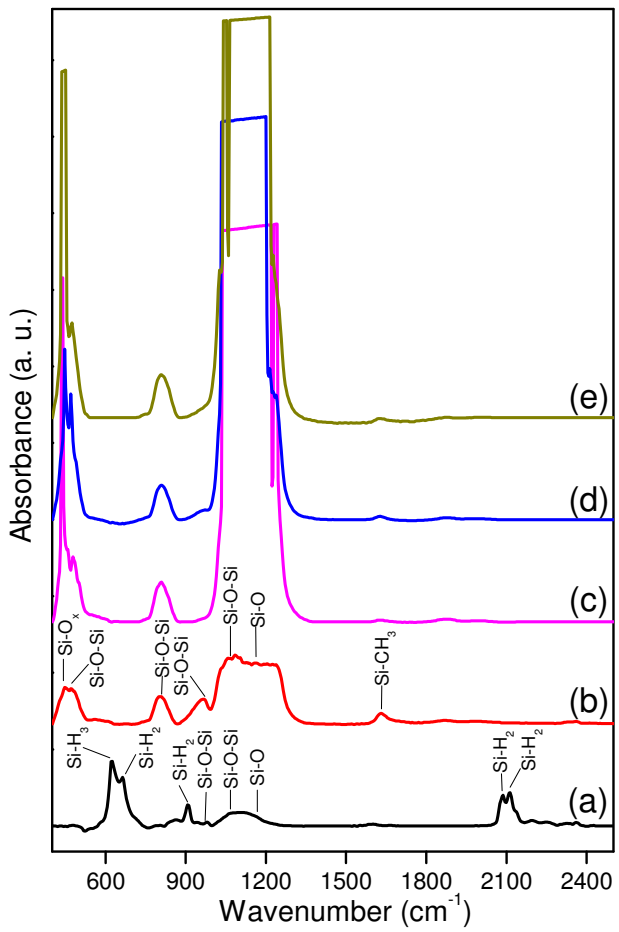

Figure 2. FTIR spectra of (a) PS reference and Ox-PS processed with the following parameters: (b) T = 800º C and t = 20 min, (c) T = 1000º C and t = 20 min, (d) T = 1000º C and t = 60 min, and (e) T = 1000º C, t = 60 min + thermal annealing in forming gas environment.

3.2 Electrical Characterization

Figure 3 shows I-V curves measured for the MOS devices fabricated from Ox-PS layers obtained with T = 1000º C. A typical Schottky electrical behavior is noted, which characterizes the semiconductor nature of the metal-oxide contact.

A leakage current about 60 nA was measured for an applied potential of 2.5 V in the device obtained with oxidation time of 20 minutes (Figure 3(a)), which is a current value relatively high for application of this oxide as insulating film in HI-PS FE device. The current level was reduced to about 7.5 nA (for the same level of applied potential (2.5 V)) in the device with oxidation time of 60 minutes (Figure 3(b)), which demonstrates that increased oxidation times can promote more densification of the films and, consequently, improve their dielectric characteristics.

Figure 3(c) shows the I-V curve obtained for the device submitted to the post-oxidation annealing (applied in the samples with better morphologic and electric characteristics (i.e. samples oxidized with T = 1000º C and t = 60 minutes)), where we can note a strong reduction of leakage current (from 7.5 nA to ~50 pA) for the same bias level as compared with the other experimented samples. The maximum current value measured was about 1.4 nA, characterized for an applied potential of 40 V, which corresponds to the voltage compliance of the equipment used in this analysis. The hypothesis for the reduction of the leakage current after thermal annealing is the passivation of trapped and free charges present in the oxide [25]. These results demonstrate that the Ox-PS obtained under Oxidation Condition D (T = 1000 ºC, t = 60 minutes and thermal annealed) is suitable for use as insulating film in HI-PS FE integrated device.

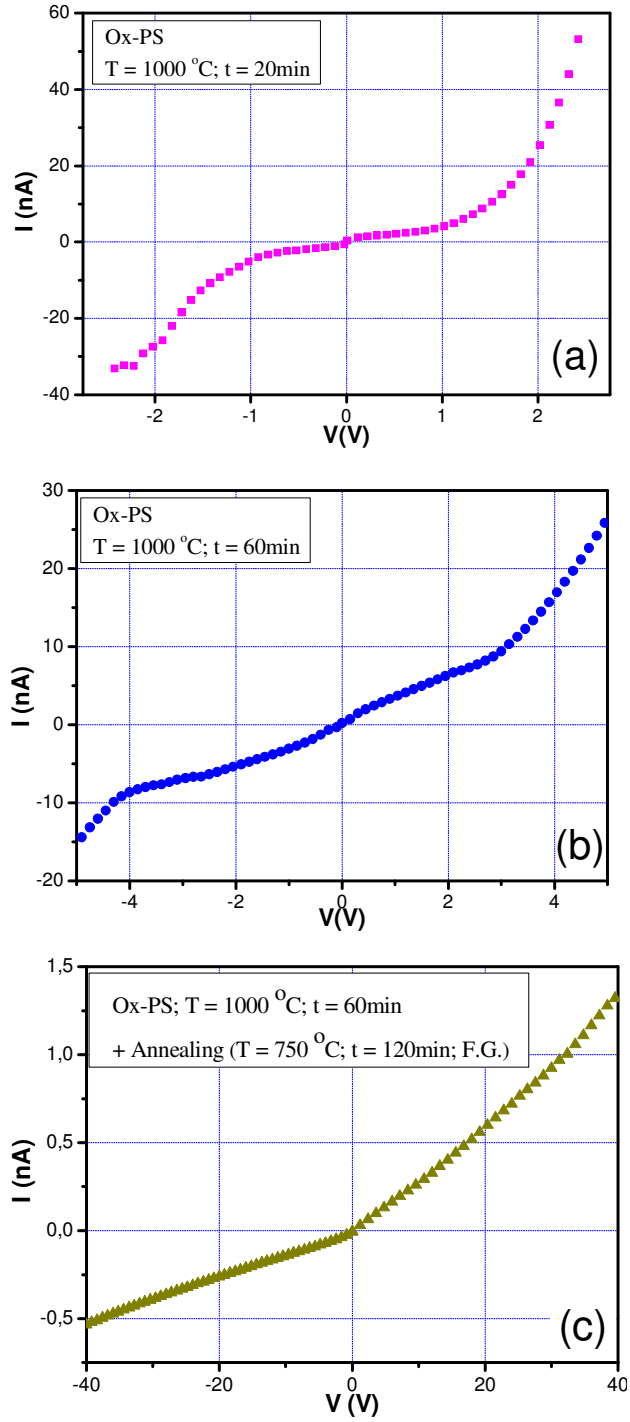

Figure 3. I-V curves from MOS devices applying Ox-PS as insulating between metal (aluminum) and semiconductor (Si p type).

4. CONCLUSIONS AND PERSPECTIVE

Thermal conditions were analyzed to promote total oxidation of PS layers. Short oxidation times (20 minutes) and low temperatures (T = 800 ºC) introduced mechanical stress in the Ox-PS films. The increase of temperature and oxidation time (T = 1000 ºC and t = 60 minutes) has avoided this problem, and allowed the obtaining of oxidized PS films free of cracks.

FTIR analysis showed the complete oxidation of PS films for all experimented oxidation conditions, which was demonstrated by the transition or replacement of silicon-hydrogen bonds to silicon-oxygen type bonds. The electrical characterization presented a reduction of the leakage current when the time of oxidation was increased from 20 minutes to 60 minutes in 1000º C, but the current value obtained with low bias (about 7.5nA for 2.5V of applied voltage) was not suitable for FE applications. After a thermal annealing process, the leakage current was strongly decreased (from nA to about 50 pA) for the same bias level, probably due to the passivation of charges present on porous oxide structure.

In conclusion, the preliminary Ox-PS results, obtained with temperatures of 1000 ºC, times of 60 minutes, and submitted to post-oxidation thermal annealing process, has potential for applications as insulating films in FE devices fabricated by HI-PS. As perspective, these oxidation conditions will be applied in the HI-PS process to obtain integrated anode-cathode structures. This implementation aims, besides the proper electrical insulation, the reduction of process steps and complexity of this technique.

5. ACKNOWLEDGMENTS

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