Secondary electron emission in nanostructured porous silicon

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Abstract. We studied the reversible reduction induced by ion bombardment of the secondary electron emission (SEE) yield. This effect has been modelled as due to changes in dynamically sustained dipoles related with ions and electrons penetration ranges. Such charge configuration precludes the escape of electrons from the nanoporous silicon, making the SEE dependent on the flux of impinging ions. Since this dipolar momentum depends on the electric conduction of the porous medium, by controlled oxidation of the nanoporous structure we change the conduction features of the sample, studying the impact on the SEE reduction effect. Li ion bombardment was also used with the intention of changing the parameters determining the effect. FT-IR and Auger electron spectroscopy were used to characterize the oxidation degree of the samples at different depth scales.

1. Introduction
Since efficient photoluminescence of porous silicon (PS) was discovered by Canham [1], this material has been extensively studied. Pores in PS can be tailored in different size scales ranging from microns to nanometers. The most interesting features appear in the nanoscopic range, where quantum effects are involved. The expected utility of PS covers a wide range of applications. An incomplete list includes its possible use as electron cold emissor [2], electroluminescent devices [3], plasma and field emission flat displays [4, 5]. To fully accomplish any of these goals, a full understanding of secondary electron emission (SEE) processes is needed. Although the physics of SEE in thin dielectric films is a matter that has been widely studied [6-8], size effects in electronic properties of nanoporous silicon introduce new features opening an interesting field of basic and applied physics.

In this work we present results for ion bombardment effects on secondary electron emission of nano, meso and macroporous, pure silicon and oxidized films.

2. Experimental details
Nanoporous silicon (NPSi) samples were prepared by anodization of monocrystalline n-type (1-10Ωcm) and p-type (7-17Ωcm) silicon substrates using a solution 1:2 HF (50%): ETOH, as electrolyte and current density of 20mA/cm². P-type samples were prepared in the dark and n-type under illumination having a luminic intensity of 140 mW/cm² provided by a dichronic lamp. In order to prepare mesoporous silicon, p-type (1-4 mΩcm) wafers were anodized using the same electrolyte and current density as for NPSi. Macroporous silicon was obtained from p-type silicon (7-17 Ωcm) using a 1:9 HF (50%): Dimethylformamide. The current density used was 3mA/cm² in this case. In all the cases the samples were rinsed with ethyl alcohol after preparation and then dried under N₂ flow. Thicknesses of the samples were estimated at around 1 μm for thin samples and 10-30 μm for the thicker ones. The thicker nanoporous samples showed crashes but they had a uniform aspect. The porosity of the mesoporous samples were estimated from the fit of the reflectance spectra taken from thin layers, using the Looyenga approximation. The porosity of NPSi was estimated using the gravimetric method. The values of porosities were around 0.9 for the nanoporous sample and 0.55 for the mesoporous samples.

The SEE spectra were measured in a PHI 590A Auger electron spectrometer, equipped with a single cylindrical analyzer. The base pressure was 2 x 10-10. To evaluate oxidation role in the studied
effect in NPSi, separated samples pieces were annealed by exposure to air in an oven at 200 ºC during periods ranging from 0 to 480 minutes. In order to compare different kind of PS samples; macro, meso and nano porous were annealed during 30 min just to stabilize them. To acquire the full spectra, the sample was polarized (-6 V). The spectra were acquired in the integrated mode, under a 400 eV - 750 nA/ mm² primary electron beam bombardment.

The sample surface was ion bombarded during SEE measurement in order to observe the reducing effect. Ion beam energy and current density was always 4 keV and 90 nA/mm². These conditions were chosen to make negligible the ion induced SEE as compared to the electron one. The oxygen amount was determined by means of Auger electron spectroscopy (AES) monitoring the O\textsubscript{KLL} transition, using the same electrons spectrometer in the differentiated way, and IR transmission spectra were obtained in an FTIR commercial spectrometer (model Spectrum RX-FTIR).

Figure 1. SEE spectra from a thick samples of NPSi (a), mesoporous silicon (b), and macroporous silicon (c). Full lines: only electron produced SEE, dotted line: SEE in the case of ion and electron simultaneous bombardment. Insets: Evolution of the maximum in SEE signal. Arrows up (down) indicates when ion gun is on (off).

3. Results and Discussion

The SEE spectra for samples exposed to the e-beam, and for the same samples exposed to both electrons and to ions are shown in Figure 1. Fig. 1 (a) shows the spectra of a ~ 30 μm thick oxidized n-type sample. When the ion beam is turned on the effect we are reporting can be fully appreciated, i.e. a strong signal decrease and an energy shift of the SEE spectrum is observed. The temporal evolution of the SEE signal, at fixed energy corresponding to the maximum of the electron induced SEE spectrum, is also shown (Insets in fig.1). The SEE reduction effect is clearly reversible. The effect was qualitatively similar in the case of unintentionally oxidized n-type nanoporous silicon. We found this effect negligible for the other tested (oxidized) samples, i.e. mesoporous (Figure 1b), macroporous (Figure 1c), and non porous crystalline silicon (not shown).

In order to reduce the ion induced energy shift effect (Fig. 1a) during the study of the signal evolution in the transient, we performed the experiments using a thinner (~1 μm) sample. The evolution of the maximum of the SEE spectrum is shown in Fig. 2 (a) for different electron beam currents. When the ion beam is turned off, the SEE signal evolves until the initial e-beam induced SEE condition is reached. Both, the initial and the final value of the SEE yields in these experiments depend on the electron beam current. The curves show an exponential behavior and can be fitted (dot lines in Fig. 2(a)) with the function:

\[ I_S = I_o \left[ 1 - A \cdot \exp\left(-\frac{t}{\tau}\right) \right] \]  

(1)
3.1 Model.

The whole behaviour may be interpreted in terms of a capacitive effect, were \( \tau \) is a time constant. The depth of electron penetration (range) is mainly determined by its energy and the solid density. The smaller the PS density, the greater the electrons range. Assuming a linear dependence we can estimate the range to be around 200 nm for 0.5 keV electrons. Being the scale size of the nanostructure in the few nm, the continuous medium approach model is valid. Therefore a negative layer is implanted deep in the PS layer.

Conversely, the range of \( \text{Ar}^+ \) ions with energies around 4 keV is around 5 nm for bulk silicon, which results of the same order or even smaller than the nanostructure dimensions, so that the range for ions in PS is similar to the silicon bulk case. Since secondary electrons emission originates close the surface, no matter the type of bombardment particle, i.e. electrons, ions, or electron plus ions, the surface layer became depleted of electrons. If only the primary e-beam is operating an internal dipole is created due to the electron depleted surface layer and negative cumulated charge at a depth defined by the impinging electron range. This process occurs for all dielectrics exposed to energetic primary e-beams \([9]\) therefore a surface positive layer and a depth negative layer are created as shown in the scheme of Fig 2(b). On the other hand, the whole energy of the primary e-beam is deposited in the region in between these layers creating electron-hole pairs, and enlarging the conductivity. Thus, a steady state in the charge distribution will be reached as a result of the electron and hole drifts induced by the internal field of the dipole. An additional charge relaxation effect will occur between the implanted negative region and the crystalline silicon substrate. This relaxation takes place slowly due to the large PS resistivity originated in the quantum confinement enlarging of the gap. Therefore, the dipolar momentum results from a dynamic balance between charging and relaxation processes.

When the ion beam strikes the sample, having the electron beam previously turned on, the positive surface charge increases due to the smaller ion range, enhancing the value of the internal dipolar momentum but without electron-hole generation in the bulk. Since the electric field near the positive surface layer preclude the electron emission, the SEE signal should decay, as it actually occurs (see Fig.1 (a)). When the ion beam is turned off, the implanted charge exponentially decay \([9]\) so the SEE yield should recover the only e-beam irradiation value, following the same rule, shown in Fig.2. Finally, considering the surface dipole as a capacitor, and taking into account that the greater the primary e-beam current the greater the e-h pairs generation and the greater the conductivity of the

![Figure 2](image-url)

Figure 2. (a) Full lines: SEE evolution for different primary electron beam current after ion gun shutdown. Dotted lines: curve fit with equation (1). The arrow indicates the sense of increasing of the electron beam current. In the inset, the evolution of \( \tau \) with the electron beam current refered to the maximum one is shown. (b) Schematic picture of the charging process during e-beam (and also ion beam) exposure.
irradiated layer, the relaxation of the charge should follow an exponential decaying with a time constant proportional to the inverse of the conductivity. Therefore the model predicts a decrease of $\tau$ with e beam intensity, as it is shown in Fig.2.

Li$^+$ ions were employed to induce the SEE reduction effect. The intention was to vary, based on the deeper penetration of Li ions as compared to Ar ones, the dipole distance between the charged regions. The effect was initially observable, but it rapidly vanished because of the doping induced by Li bombardment into the NPSi structure. This effect strongly supports the idea that the conductivity of the surface layer plays a fundamental role in the existence of the effect.

3.2 Structure effect.

Due to the fractal nature of the PS nanostructure, the characteristics of the surface remain essentially the same after ion bombardment and thus effect remains after long term ion bombardment.

The mesoporous and the macroporous samples have larger conductivities than nanoporous silicon one, allowing a faster charges rearrangement, turning negligible the surface charge and the induced dipole. Thus, this model predicts that the ion induced SEE reduction should operate for nano but not for meso and macroporous samples as we actually found in our experiments (Figs.1 a and b).

3.3 Oxidation effect

NPSi oxidation affects its conductance in two ways; the macroscopic conductance decreases due to the growth, at the expense of silicon, of an insulator phase of silicon oxide. On the other way, since dimensions of nanostructures are in close relation to the degree of oxidation of NPSi samples [10] the confinement gap increases lowering the conductivity.

Oxidation effects were studied in a detailed way through electron induced SEE spectroscopy with and without bombardment from p-type NPSi samples thermally oxidized in air at 200°C. These samples were preferred due to its larger stability as compared to n-type ones.

For oxidation experiments, different fragments of the same p-type NPSi were isothermal annealed during different time intervals (up to 8 hours) at atmospheric pressure, being one of them loaded into the spectrometer immediately after fabrication, i.e. with no annealing. The oxygen amount was checked by AES and FT-IR, showing both techniques the same evolution. Since FT-IR monitors the whole sample whereas AES sees only a very narrow region near the surface we infer that oxygen is incorporated uniformly inside the porous layer.

Fig. 3 shows the reversible reduction coefficient -defined as the relative change of the SEE produced by ion bombardment- versus the oxygen content -evaluated by integration of the stretching band of Si-O bonds in siloxane bridges. As it can be observed, more oxidized samples show larger reduction effects. In the inset of Fig. 3 we can see higher SEE for stronger oxidized samples. The behavior shown in this figure supports our idea that larger dipole means larger reducing effect.

**Figure 3.** Signal reduction coefficient versus oxygen content. In the inset: SEE signal as a function of the oxygen content.
3. Conclusions
In NPSi samples a reversible reduction in electron induced SEE exists when simultaneous bombardment with ions occurs. This phenomenon can be understood as the result of stationary dipoles modification coming from the balance between generation and recombination of carriers by charged particle bombardment. The difference between ion and electrons ranges has an important role in the kinetics of SEE variation. The reduction in secondary emission is more important for oxidized samples, and turns to be reversible due to nanoporous structure fractal feature.

5. References
[1] Canham LT 1990 Appl. Phys. Lett. 57 1046
[2] Takai M, Yamashita M, Wille H, Yura S, Horibata S, and Ototake M 1995 Appl. Phys. Lett. 66 4
[3] Koshida N, Sheng X, and Komoda T 1999 Applied Surface Science, 146, 371
[4] Tam HL, Kung EW, Zhangb XX, Gongb ML, Cheah KW 2003 Optoelectronics Proceedings of the Sixth Chinese Symposium 120
[5] Kleps I, Nicolaescu D, Lungu C, Musa G, Bostan C, Caccavale F 1997 Applied Surface Science 111 228
[6] Fitting HJ, Cornet N, Touzin M, Goeuriot D, Guerret-Piécourt C, Tréheux D 2007 J. of the Eur. Cer. Soc. 27
[7] Xue-Chun Li, You-Nian Wang 2006 Thin Solid Films 506–507 307
[8] Baragiola RA 1982 Radiation Effects 61 47
[9] Thiel BL, Toth M 2005 J. Appl. Phys 97 051101
[10] Koropecki RR, Arce RD, Schmidt JA 2004 Phys. Rev. B 69 205317