Switchable Electric Field Induced Diode Effect in Nanostructured Porous Silicon

Oscar Marin, Raul Urteaga, David Comedi, and Roberto R. Koropecki

***Abstract*— Unidirectional current flow (diode-like behavior) is observed in Al/Nanostructured Porous Silicon/Al structures (Al/SP/Al) after applying a forming electric field (E) for a long time. We found that rectifying characteristics depend on the direction of E. The forward direction coincides with the direction of E. The diode direction switches when E is inverted. The rectification factor passes from 200 to 26 from one direction to the other, the effect is reversible and can be repeated several times.**

***Index Terms*— Metal/semiconductor interfaces, porous silicon (PS), switchable diode effect.**

I. Introduction

RECENTLY, materials exhibiting phenomena associated with electrical memory properties aroused considerable interest in the scientific community. This is due to the possibility of designing devices for storing information and because of interesting physical phenomena associated with these effects. Indeed, resistive switching, electrical hysteresis, and negative differential resistance are reported for porous silicon (PS) devices [1]–[3].

Recently, a switchable diode effect controlled by short high electric field pulses is reported for ferroelectric materials [4]. This effect is not observed for silicon devices and is rarely reported for other materials.

The physical mechanism behind the switchable diode effect remains unclear [5], [6]. For ferroelectric materials, it is associated to the generation of field controlled space charge regions within contact/ferroelectric interfaces [7], [8]. The most accepted model considers band bending effects in contact/ferroelectric interface caused by a space charge region that modulates the Schottky energy barrier [5], [9], which limits the injection of carriers [6]. The space charge region is associated with oxygen vacancies that migrate from a contact interface to the opposite one because of ferroelectric polarization [5]–[8]. The switchable diode effect has a technological interest, because of potential applications in the design and fabrication of memory devices [6], [7], [9].

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In this letter, we demonstrate a switchable, electric field induced, diode effect in PS films with Al contacts. We study the influence of the electric field strength and duration, and of the PS film thickness, on the effect, and propose a possible mechanism to explain the observed results.

II. Experiment

The PS films are fabricated by electrochemical anodization [10] of crystalline p-Si ($\rho = 2 - 4$ mΩ·cm) with <100> orientation. The crystalline silicon wafers are etched in a solution of HF (50%):Ethanol 1:2 with a current density of 20 mA/cm^2. The resulting films are mesoporous (pore size of 5–10 nm) with porosity of 60%. The anodization times are adjusted to obtain PS films with thicknesses of 750, 1500, and 3000 nm.

The PS films are separated of the silicon substrate by etching in a 1:7 HF (50%):Ethanol solution using a short pulse of high current density (360 mA/cm^2). In a wet medium, such thin free-standing PS films can be transferred to another substrate [11]. Thus, the PS layers are transferred to aluminum-coated glass slices. The transferred layers are dried under N_2 flow, forming mechanical Al/SP bottom contact. Top contacts are made by vacuum evaporation of aluminum.

The as-prepared devices are placed in a vacuum chamber at 5×10^{-5} Torr remaining there during 8 h before starting the experiments to degas the porous network.

Constant voltages are applied to the devices during a given time. After that, I–V curves are measured ranging from -1 to $+1$ V to characterize electrical response. The I–V curves are measured following a voltage sweep: 0 V $\rightarrow$ 1 V $\rightarrow$ -1 V $\rightarrow$ 0 V. The positive sign refers to the polarization of top contacts. The inversion grade (IG) is defined as the absolute value of the ratio between the current measured at $+1$ V and the current measured at -1 V.

III. Results and Discussion

A diode-like behavior is observed after applying $+5$ V during a relatively long time (3000 s) to a device with a PS film thickness of 750 nm (forming electric field $E = 66.6$ kV/cm), The resulting forward diode direction is as that of the applied electric field. When the E direction is inverted by applying -5 V for 3000 s, the diode direction is also inverted, showing a switchable diode effect. This diode-like behavior is not an intuitive result, because the top and back contacts are symmetric interfaces (Al/PS) and

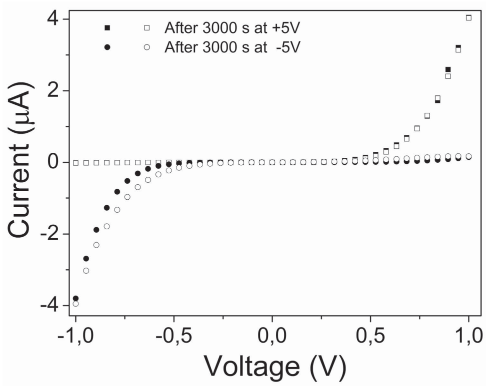


Fig. 1. I–V curves after applying +5 V during 3000 s (squares), and after applying −5 V during 3000 s (circles). The filled symbols: 0 → 1 V and −1 V → 0 sweep and open symbols: 1 V → −1 V sweep. The acquisition time between points is 1 s.

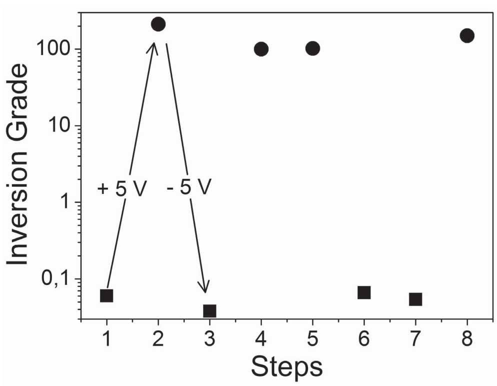


Fig. 2. IG for consecutive experiments. Circles: IG for state after applying +5 V. Squares: state after applying −5 V. In all cases the forming time is ∼3000 s. From 4 to 5 the applied voltage is +5 V again, and from 6 to 7 it repeated the −5 V polarization. In both cases no significant current changes occur.

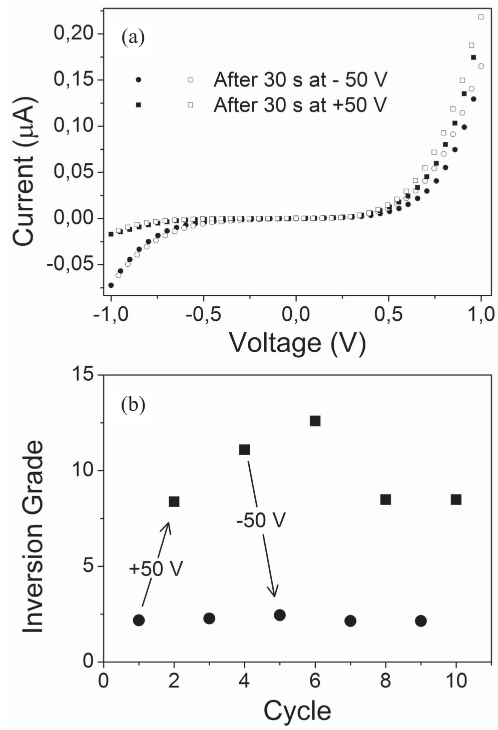


Fig. 3. (a) I–V curves after applying ±50 during 30 s. Filled symbols: 0 → 1 V and −1V → 0 sweep. Open symbols: 1 V → −1 V sweep. The acquisition time between points is 1 s. (b) IG for a consecutives experiments.

the energy barriers should have similar values. The diode-like behavior and switchable effects are only observed under vacuum for devices with PS thicknesses of 750 nm. No effects are observed for devices with PS thicknesses of 1500 and 3000 nm after forming times as long as 4000 s with 5 V of forming voltage. This indicates a relationship with the porous layer thickness, although more experimental work should be made to determine the functional dependence.

The I–V curves for diode-like behavior and switchable effect are shown in Fig. 1.

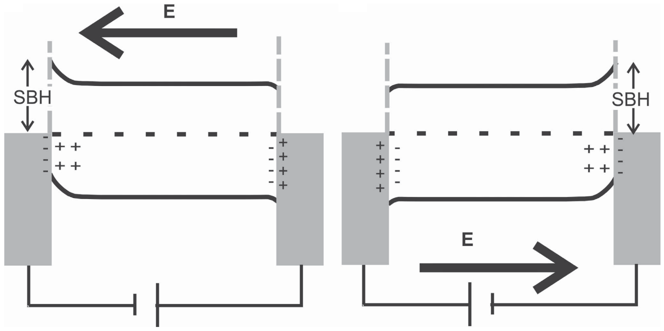
In Fig. 1, the IG value for the diode formed after applying +5 V is ∼220 and 1/26 for the diode formed after applying −5 V. Fig. 2 shows the IG values obtained for consecutives experiments alternating the E direction (±5 V for ∼3000 s), showing that the switchable effect can be cycled and reproduced several times. No effect is obtained after a second step maintaining the same E direction (steps 5 and 7 in Fig. 2).

To reduce the forming time needed to observe the diode-like behavior, we increase the E value to 666 kV/cm (50 V). The I–V curves obtained after polarization during 30 s with +50 V and −50 V are shown in Fig. 3(a). As it can be observed, 30 s it is enough time to produce a measurable switching effect when ±50 V are used for polarization. Fig. 3(b) shows the IG values for consecutives experiments alternating the direction of E. In this case, after +50 V, the IG is about ten and changes to two after −50 V.

According to our results, it is reasonable to suggest that the energy barriers between PS and aluminum electrodes are changed by the E. When an E is applied, the PS/Al Schottky barrier height (SBH) can be modulated by redistribution or change of space charge regions nearby to interfaces.

Our PS is in a nonluminescent state, which is known to be a characteristic property of materials behaving as intrinsic or slightly n-type doped semiconductors, even for PS films prepared from p-type crystalline silicon [12]–[14]. Based on this and on the SBH modulation hypothesis, in Fig. 4 we present a possible band structure for Al/PS/Al devices to describe the switchable diode effect. When an E is applied on the Al/SP/Al device, a negatively charged region on one of the interfaces may be generated, causing a downward band bending and a decrease of the SBH, enabling the electron flow. Simultaneously, in the opposite interface, an upward band bending is induced, causing an increment of the SBH.

However, to originate a diode-like behavior and switchable diode effect in the Al/SP/Al device, a mechanism responsible for the symmetry breaking of the contact interfaces should be invoked. Similar to ferroelectrics [5],[6], a potential mechanism in PS could be associated to the electromigration of species chemisorbed at the silicon nanostructure surfaces comprising the PS. As no annealing is made before top contact evaporation, water or ethanol may be present. However, the pore surfaces are rich in hydrogen [10] and consequently it is



(a) (b)

Fig. 4. Band structures for both diode polarization states.

a better candidate for electromigration in PS. The capability of hydrogen to migrate under influence of an external electric field at semiconductor surfaces is demonstrated [15]. Although we expected a low incidence of surface electromigration at room temperature, the large specific surface of the PS may favor a measurable effect. A change of the hydrogen concentration near the electrodes, induced by the electric field, could explain the switching effect.

This mechanism is in accordance with the need for long forming times to completely establish the diode behavior, as well as this effect occurs only in devices with thin porous layer. The slow hydrogen mobility through the nanowires surface requires applying high E for a long time to produce a measurable effect.

New experiments are carried out to test the hypothesis of hydrogen electromigration. It is possible to achieve the hydrogen desorption when the device is annealed under vacuum and to study the rectifying behavior as a function of hydrogen content.

IV. Conclusion

A switchable, electric field induced, diode effect was observed in Al/PS/Al device. The effect occurred for sufficiently thin PS layer, high electric field and long time, indicating that electromigration of chemisorbed species (probably H) may be the mechanism behind the experimental results. A band structure model was presented, which schematically described SBH changes that followed space charge redistributions at the Al/PS contacts interfaces induced by the applied electric field.

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