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Formation and characterization of porous silicon films obtained by catalyzed vapor-chemical etching

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ABSTRACT

Porous silicon films obtained by the metal-assisted vapor-chemical etching technique have been characterized. For the film formation, epitaxial (100) N/P^+, 1–5 Ω cm monocrystalline silicon wafers were used. The vapors of an alcoholic solution of H_2O_2/HF were drawn towards the silicon surface, which was previously covered with a thin layer of gold (~8 nm) for the catalytic etching. For the optical and morphological characterization of porous films, Raman spectroscopy, Ellipsometry, FTIR spectroscopy and SEM images were used. The films thickness kept a linear relationship with etching time. A porosity gradient from the surface towards the interface (65% to 12%) was observed in the films. A large amount of Si–H bonds as related to O–Si–O bonds were observed and the pore size depends on the HF concentration. Irregular morphology was found in films formed with 50% HF.

1. Introduction

In the literature there are a large number of papers focused on Porous Silicon (PS) formation and its optical, insulating and chemical sensing applications [1]. The ability of the PS to adsorb gaseous species [2] is due to its high surface chemical activity and a great surface to volume ratio greater than 200 m^2/cm^3 [3], which is suitable for sensing applications.

Since the PS discovery by Uhlir and the subsequent works of Canham on its properties in 1990 [4,5], the electrochemical etching technique has been used for many applications of PS rather than other methods such as the chemical etching, therefore motivate us to make this work.

In this paper, we use the chemical etching method, particularly the metal-assisted etching technique [6,7]. This technique has the advantage of being easy to implement, requiring neither biasing nor illumination sources, in addition to being able to form PS on N-type and P-type silicon. It is also selective, since it allows etching only on the areas covered by the metallic film, which catalyzes the etching reaction and it can be produced at room temperature. However, some disadvantages of this method are its low reproducibility an irregular PS/Si interface and high formation ratios (about 15 nm/s or greater). This last disadvantage is overcome by performing the etching with the vapors of the solution, rather than immersion, in analogy to the procedure used by Saadoun et al. [8]. As mentioned, this technique uses as a catalyst either a nanometric film (~10 nm), or nanoparticles [9] of Au, Pt, Pd or Ag. These can be deposited by either physical or chemical methods. The silicon surface is then exposed to the vapors of the etching solution, which is composed of Ethanol, Hydrogen peroxide and Hydrofluoric acid. The overall chemical reaction for the formation of the PS is given as [6]:

$$Si + H_2O_2 + 6HF \rightarrow 2H_2O + H_2SiF_6 + H_2\uparrow \quad (1)$$

The presence of PS on the silicon substrate is observed as a color change of its surface, indicating a decrease of the refractive index in contrast to the one of crystalline silicon [10], initially from 3.89 and decreasing down to values close to 1.5 at 632.8 nm, as determinate by ellipsometry, allowing also deduct the optical thickness. The thickness of the porous layer is associated with the etching depth, and is equal when the dissolution of a thin surface layer does not occur. Additional studies made to characterize the PS films were: Raman and FTIR spectroscopy in order to determine the chemical composition, and SEM microscopy to study surface morphology. The PS/Si junction can also be electrically characterized, but this will be reported in another work.

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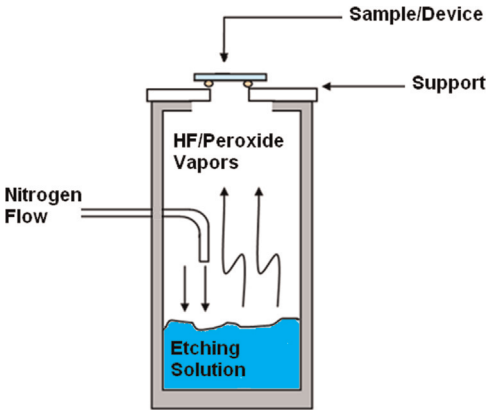

Fig. 1. Schematic cross sectional of the vapor-chemical etching reactor.

2. Experimental details

Monocrystalline epitaxial N-type (100) silicon layers on P^+ substrate were used to obtain the PS films. Epilayers were 4 μm thick and 1–5 Ω cm resistive. The standard RCA technique was used for cleaning the substrates. It was followed by the deposition of a thin layer of Au (~8 nm), using an Argon plasma DC sputtering process under the following conditions: 10^{-2} mbar pressure and 10 W power for 30 s. Analytical grade: ethanol C_2H_5OH (99.9% purity), hydrogen peroxide H_2O_2 (30% purity), and hydrofluoric acid HF (49% purity) were used for preparing the solutions. 20 ml from three different etchant solutions with ratios: A=(40:50:10), B=(40:35:25) and C=(20:30:50) v% respectively were used in this work. The samples were mounted 20 cm apart from the solution surface and then exposed to the vapors under a constant N_2 flow of 2.3 l/min as carrier gas. The reactor was manufactured with Teflon and is similar to that used in reference [8], but in our version the solution was kept at room temperature (20 °C), see Fig. 1. The corresponding concentrations in the vapor phase are shown later in the Table 1 and depend on their vapor pressure. The etching time was set at one and two hours for each of the different etching solutions. In order to stop the etching process, the samples were rinsed in 2-propanol and acetone, and dried with a nitrogen flow. We obtained six types of films, labeled as MR1, MR2, MR3, MR4, MR5 and MR6. Odd-labeled samples set were etched for one hour and pair-labeled samples set were etched for two hours, MR1 and MR2 were formed with 10% HF, MR3 and MR4 were etched with 50% HF, MR5 and MR6 were formed with 25% HF. Two additional PS samples, MR7 and MR8 have been formed using only the solution A with etching times of three and four hours.

3. Characterization and results

3.1. Ellipsometry

The PS films were subjected to optical and morphological analysis. Ellipsometric characterization was performed by means of a variable angle ellipsometer (VAE) Gäertner L2W16S366 that uses a 632.8 nm wavelength He–Ne laser. The optical thickness and refractive index were determined by fitting the measured ellipsometry angles Δ and Ψ, to a three-layer model; layer 1 at the surface, layer 2, intermediate and layer 3 at the interface with silicon substrate.

Fig. 2(a) shows the thickness dependence of each layer with the HF concentration in the etchant solution, for the three-layer model of ellipsometry. Layer 1 has a slight variation in thickness between 94 nm and 136 nm, showing scarce dependence with the time at low HF concentrations and it is slightly more dependent with the etching time at highest concentrations. The thickness of the layers 2 and 3 depends much more on the etching time than on the HF concentration.

Fig. 2(b) shows the refractive index values of each layer in the model versus the HF concentration in the solution for both etching times. Small differences between refractive indices corresponding to different times and HF concentrations are observed, except in the cases of layers 1 and 3 corresponding to 50% HF in the solution. A low refractive index at the PS surface (layer 1) and a higher one near the PS/Si interface (layer 3) are observed. This leads us to consider that the PS film refractive index changes gradually with the depth in the film.

The porosity in a film is given by the volume fraction occupied by air. Porosity values were obtained with the help of the Bruggeman effective medium theory [11], using the Eq. (2) and considering mesoporous films, where n_{Si} and n_{PS} are the refractive index of silicon and porous silicon respectively. Table 1 shows the total thickness of the films, d_{FT}, and the porosity of each layer (P_i) of the model.

$$P = 1 - \frac{\left(1 - n_{PS}^2\right)\left(n_{PS}^2 + n_{Si}^2\right)}{2n_{PS}^2\left(1 - n_{Si}^2\right)} \tag{2}$$

The porosity gradually decreases from the surface (~60%), exposed to the constant etching of the HF vapors, towards the interface (less than 12%), which corresponds to the pores bottom. Porosity is not dependent on HF concentration in the etchant solution; this is clearly shown by the values in Table 1. The total thickness keeps an approximate linear relationship with etching time, obtaining an etching rate in the order of 1 μm/h. In Fig. 3 the thickness dependence on the etching time can be seen.

3.2. Raman spectroscopy

The measurements were made with a Horiba–Jobin Microprobe Yvon HR800, which uses as excitation source a He–Ne laser

Table 1
Total thickness and porosities P_i for each layer in the model of the PS films, considering mesoporous films.

Sample	Solution %HF	Vapor %H_2O_2:HF	Time (h)	d_{FT} (nm)	P_1 (%)	P_2 (%)	P_3 (%)
MR1	A 10%	0.47:0.21	1	951.85	65.13	27.36	16.33
MR5	B 25%	0.33:0.52	1	958.27	61.03	31.25	17.02
MR3	C 50%	0.28:1.05	1	961.41	61.27	30.24	16.31
MR2	A 10%	0.47:0.21	2	2144.74	62.14	28.00	12.45
MR6	B 25%	0.33:0.52	2	1838.71	58.60	28.62	17.35
MR4	C 50%	0.28:1.05	2	2325.98	67.38	31.19	7.36
MR7	A 10%	0.47:0.21	3	3104.1	–	–	–
MR8	A 10%	0.47:0.21	4	4245.3	–	–	–