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Black-silicon production process by CF_4/H_2 plasma

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ABSTRACT

Nanoscale structures in silicon have been produced by means of a maskless plasma process that employs tetrafluoromethane and hydrogen. The influence of the radio-frequency power and process time on the surface texturing was studied. Desirable texturing effect has been achieved by applying an RF power in the range of 200–280 W and process time in the range of 20–30 min. The textured surface is characterized by nanopillars with lateral dimensions ranging from 50 to 300 nm and with a depth in the 100–300 nm range. Depending on process parameters in the plasma etching recipe, the optical reflectance of the silicon surface is lowered and R < 5% is reached in the range going from the visible to the near-IR region.

1. Introduction

The physical structuring of silicon is one of the cornerstones of modern microelectronics and integrated circuits. Regarding Silicon-based optical detectors and solar cells, the high reflectivity at input surface can hinder efficient light collection. Surface texturing is one way to minimize unwanted reflections and lately, the anti-reflection effect of the Si surface texturization has been particularly studied in view of light absorption enhancement in solar cells [1–4]. The texturing of the Si surface was also proved to be effective in functionalizing it as a scaffold for biomedical applications, by providing selective antibacterial characteristics [5]. In these fields of application, the realization of high-aspect-ratio vertical features on Si substrates is the crucial step in the fabrication process. For this purpose, laser-based manufacturing processes have been proposed and developed [2,6]; wet chemical etchants can also be exploited to create anisotropic profiles, because they are cost-effective and easy to use, but not environmentally friendly. The use of dry processes instead of wet has been strongly supported in recent years, and dry plasma etching has become a conventional technology in microelectronics. In particular, halogen-based plasmas have been extensively used for Si etching. What is usually seen as an undesirable effect in plasma etching is surface roughening, which can usefully be controlled to induce Si texturing under certain experimental conditions. The Si texturization has been studied mainly in fluorine-based plasmas by exploiting the random automasking effect on surface during the etching. It has been demonstrated that the automasking effect is obtained if a random passivation is generated during the etching [7]. The passivation is essential for protection of sidewalls and obtaining vertical features. C_4F_8 gas has been used as the reactant to produce a polymeric passivation layer which protects the trench sidewalls realized in the etching process by fluorine based gas such as SF_6 [8–9]. Maruyama et al. reported a texturization process which employed SF_6 plasma in the etching process and a mixture of O_2 gas during the passivation step [10]. It is worth mentioning that the latest process exploits a low-density plasma power and no polymeric passivation is needed, instead a growing SiO_xF_y layer is formed during the passivation step. In this paper, we report on the development of a method, based on hydrogen in place of oxygen, for the formation of the passivation layer. The purpose of this research is the fabrication of nano-structures on Si substrates, to be used either to enhance light absorption for opto-electronics and photovoltaic applications, or to provide patterned surfaces for bio-medical applications. The process is realized in a low-density capacitively-coupled plasma RIE reactor in CF_4/H_2 mixture.

2. Experimental

2.1. The plasma reactor

An RF plasma system [11] has been used to produce a physical structuring of Silicon (type P, dopant B, <100>, 0.01–0.02 Ω-cm, 1 × 1 cm^2, thickness = 400 μm). The experimental apparatus consists of a

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parallel-plate, capacitive-coupled system, consisting of a cylindrical stainless steel vacuum chamber with an asymmetric electrode configuration. A powered electrode (3-in. diameter) is connected to an RF (13.56 MHz) power supply, coupled with an automatic impedance matching unit, while the other electrode (3-in. diameter), consisting of stainless steel, is grounded. Si substrates are placed on the powered electrode at 6 cm away from the ground electrode. The substrate temperature is monitored by a thermocouple fixed directly on the substrate. Before the process, the substrates are cleaned by chemical etching solutions (alcohol followed by rinse in deionized water) to remove surface contaminants. The Atomic Force Microscopy technique has been used to check the surface roughness of substrates after cleaning. The RMS roughness was in accordance with manufacturer's data (≤1 nm). The process chamber is pumped to a base pressure below 1×10^{-5} Pa and high-purity reactive gases (CF_4 and H_2) are introduced into the vacuum chamber through a mass flow controller in order to establish the desired working pressure, which is fixed at 10 Pa. The plasma phase has been characterized through optical emission spectroscopy. The experimental apparatus consists of a scanning monochromator (Horiba JobinYvon iHR550) of the Czerny–Turner type, with a focal length of 0.55 m, built around a holographic diffraction grating with 1800 grooves/mm, coupled with a CCD (Synapse Horiba JobinYvon) camera, and thermoelectrically cooled to −70 °C. The optical emission from the plasma is collected from the bulk volume of the discharge through a quartz window by a plane-convex convergent lens of 1 in. diameter and conveyed by an optical fiber (length 3 m, core 600 mm, numerical aperture 0.22) onto the entrance slit of the monochromator, keeping the slit aperture fixed at 50 μm.

2.2. Coating characterization

The nano-structured samples have been characterized for their total optical reflectance (sum of normal and diffuse reflectance) in the spectral range of 250–1100 nm by means of a spectrophotometer (Perkin Elmer LAMBDA 1050 UV/Vis/NIR), equipped with a 150 mm diameter integrating sphere.

Different surface analysis methods were performed to investigate the morphology and chemical properties of the nano-textured samples. HI-resolution SEM imaging was performed using a Tescan MIRA III Field-Effect SEM. The surface chemical characterization was carried out by means of X-ray photoelectron spectroscopy (XPS). The core level spectra were acquired using a non-monochromatized Al anode X-ray source ($h\nu = 1486.6$ eV) VSW model TA10 and a hemispherical analyzer VSW model CLASS 100, equipped with a single channel detector, operating in constant pass Energy mode (22 eV) with 0.9 eV of overall resolution. Wide scan spectra were acquired with 2 eV of overall resolution. All spectra were referenced to the same energy scale determined by calibrating the Ag 3d5/2 line at 368.3 eV. In order to clarify the formation mechanism of nanostructures on Si surface, Scanning Auger Micro-spectroscopy (SAM) was used to complement XPS analysis. The purpose is to provide additional information about the selective etching process by locally measuring the elemental composition in different spots of the textured surface. Auger electron spectroscopy probes the elemental composition of surface layers, as well as interfaces and grain borders, down to a depth of about $1 \div 2$ nm with a sensitivity of about 1% at., while the lateral resolution is set by the diameter of the electron beam [12]. In the present work, the SAM system (PHI 660) was operated at e-beam acceleration voltage V = 10 kV, e-beam current I = 32 nA and analyzer energy resolution ΔE/E = 0.5%.

3. Results and discussion

3.1. Texturing process development

Under suitable plasma conditions [13–14], the fluorocarbon molecules undergo fragmentation and ionization, and the main species produced are CF_x and F, of which the most useful to the purpose is the Fluorine species. When an F atom hits the substrate, it can remove a Si atom. By chemical reaction of F with Si, a volatile SiF_4 gas is created and then pumped out of the chamber. The etching is predominately a chemical etching, so the control of the F density in chamber strongly affects the etching rate. The main parameters to control the F density include RF power, gas flow rate, pressure and different dilution of gases. In order to tune the texturization process based on the hydrogen content, we have rated the fabrication of nano-structures as a function of RF power and gas concentration. As is well-known [15], the fragmentation and ionization processes of the molecules are increased as the RF power increases. This means that the density of F atoms and the etching rate increase as a function of power (Figs. 1–2). Fig. 2 shows the collected emission by OES of main $3s^2P$ (703.7 nm) fluorine line [16] as a function of H_2 concentration and RF Power. A strong correlation between the etching rate and F density as a function of RF power was found (Fig. 1). OES results also show that the atomic fluorine concentration in CF_4 plasma increases as a function of H_2 concentration (Fig. 2).

The fluorine emission trend reported in the Fig. 2 may seem in contradiction to the well-known process that involves the recombination of H with F to form HF, thus resulting in a decrease of the F concentration as hydrogen concentration increases [17]. However, the addition of H_2 also simultaneously plays an important role in the fragmentation of CF_4 [18], generating a higher density of F radicals. Actually, at small amounts of H_2 the fragmentation process predominates over the recombination. Fig. 3 shows the Si etching rates at 200 W (4.3 W/cm^2) of power applied to RF electrode, as a function of the H_2 concentration in the feed gas. After an initial increase, the etching rate decreases at H_2 percentages higher than ≈5%. At first sight, this could be in contrast with the rationale given for Fig. 2, where the intensity of F radical monotonically grows with the increase in hydrogen concentration. However, the trend observed in Fig. 3 can be explained by considering that the etching rate of Si in fluorocarbon plasmas depends on the competition between the etching itself, due to the action of fluorine, and the deposition of CF_x radicals onto the surface. Therefore, the action of the H_2 concentration on the kinetics of the overall process can be synthesized by plotting the ratio of F/CF_x intensity, as determined by the OES signals vs. H_2 concentration (Fig. 3, right).

Namely, CF_2 is used as a representative radical for deposition [19]. The F/CF_2 ratio gradually increases with increasing H_2 content until the latter reached ≈10%, and then it monotonically decreases. The measured trend of the F/CF_2 ratio and the measured trend of the etching rate both show a similar behavior as a function of H_2 concentration, as shown in Fig. 3. Moreover, the maximum for the etching rate and the maximum of the F/CF_2 ratio approximately correspond both to a Hydrogen concentration of ≈10% H_2.

Beyond the main etching process, at the same time, a passivation layer can be created with H particles, CF_x radicals and the partially etched product SiF_x. In certain experimental conditions, the

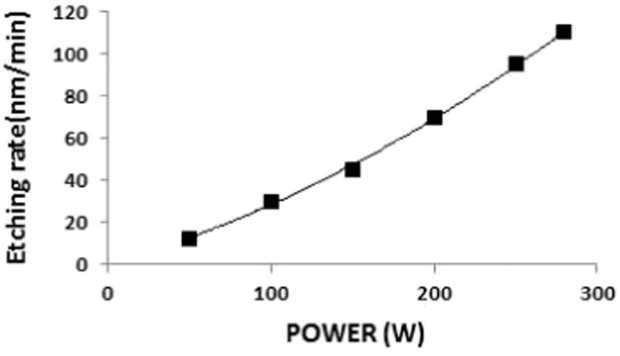

Fig. 1. Etching rate as a function of RF power in H_2/CF_4 plasma with 2 sccm of H_2 dilution (Etching time 10 min).