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Microscopic Si whiskers

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ABSTRACT

Physical properties of microscopic silicon whiskers formed by reactive ion etching in chlorine plasma are reported in an attempt to clarify the formation mechanism and the origin of the observed optical and electrical phenomena. The silicon whiskers with diameters of well under 5 nm exhibit strong photoluminescence (PL) both in visible and infrared, which are related to quantum confinement, near band-edge and defects. Vibrational analysis indicate that disorder induced LO–TO optical mode coupling is very effective. Electric field emission properties of these microscopic features were also investigated to determine their potential for advanced technology applications.

1. Introduction

Microscopic silicon whiskers, or black silicon have already been observed during the formation of Si trenches by reactive ion etching (RIE) in fluorine, bromine and chlorine plasmas [1]. However, detailed mechanism of the black Si formation and its properties are yet to be understood. It is widely believed that the formation of microscopic pillars during RIE is due to a local variation of the Si etch rate. This variation in etching rate can be caused by Si surface itself, for example inhomogeneous oxide layer or incompletely removed native oxide. The plasma tool and plasma source can be a cause of a micro-masking material e.g., by products of sputtering and re-deposition of plasma chamber electrodes and masking material [2–4]. Also, it was shown that Si nanowhiskers could be formed on untreated Si (1 0 0) using electron beam thermal annealing [5]. According to these studies, native oxide layer is undergone a thermal decomposition, which occurs through the formation of voids in the oxide layer [6,7]. The void growth occurs via the interfacial reaction between Si and SiO_2 resulting in SiO monomers which diffuse to the void perimeter. It is the purpose of this work to advance our knowledge in this field by providing new data on black Si formation and evolution.

2. Experimental

In our work, the microscopic Si whiskers were formed by RIE of p-type Si (1 1 1) and Si (1 0 0) wafers using chlorine plasma. The process leads to the formation of microscopic whiskers or black Si on all over the surface of Si wafer since it soaks all the white light (see TEM image in Fig. 1). Transmission electron microscopy (TEM), spectroscopic ellipsometry (SE), Fourier transformed infrared spectroscopy (FTIR) and photoluminescence (PL) measurements were carried out in order to investigate physical properties of the pillars. TEM bright field analysis indicates the presence of nanostructured crystalline Si whiskers with sizes well under 5 nm at tips and with lengths of up to 500 nm. Electric field emission (EFE) diodes were fabricated on Si whiskers with circular contacts (20 nm Au front and 200 nm Al back contact) in a parallel plate configuration providing better insight on the carrier transport mechanism. The active device area and the distance between electrodes are 0.3 cm^2 and 200 µm, respectively.

3. Results and discussion

TEM analysis indicates that Si whiskers are all crystalline as shown in Fig. 1a and b. Energy dispersive spectroscopy (EDS) analyses show that the microscopic whiskers are encapsulated by an ultra thin oxide layer. EDS probes 4.5 at.% oxygen which confirms the presence of a native oxide (SiO_2 or SiO_x, $1 < x < 2$) on the whiskers. The oxide layer is also confirmed by TEM and FTIR through the Si–O bondings. The whiskers so fabricated have

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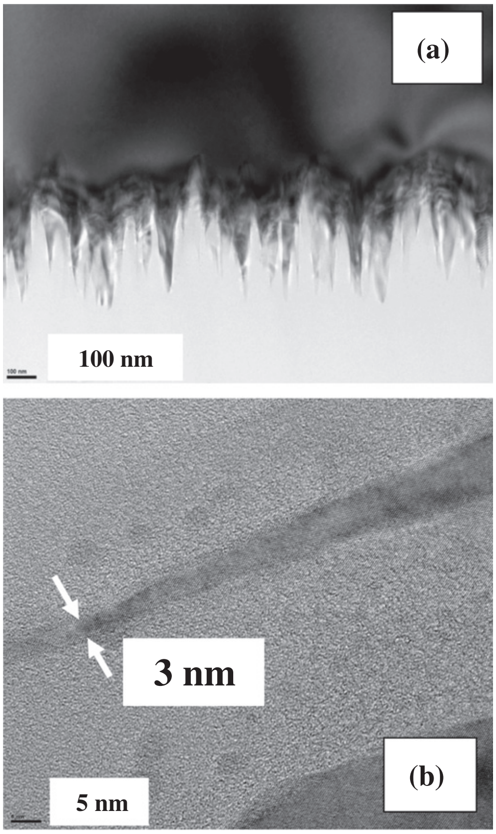

Fig. 1. A typical TEM image of microscopic Si whiskers (a) and a single silicon whisker exhibiting Si crystalline structure (b).

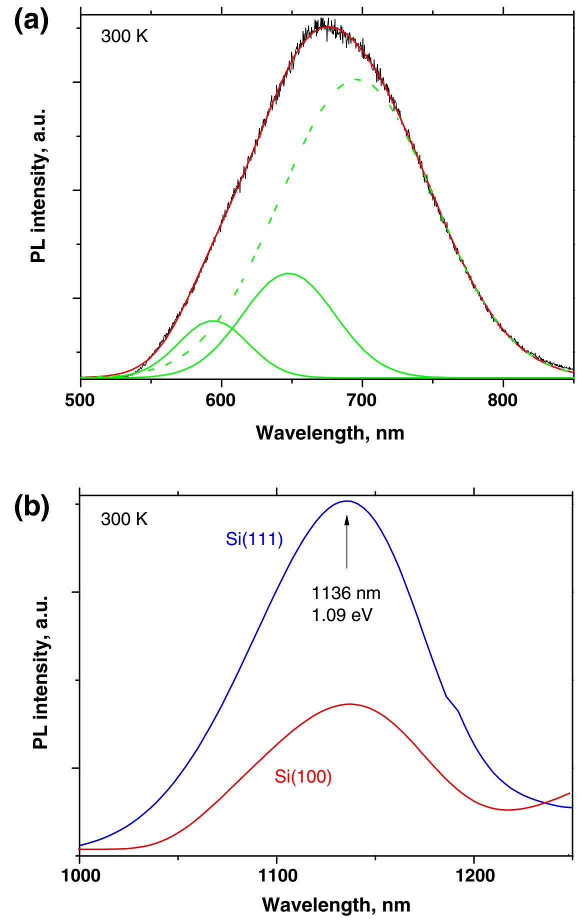

Fig. 2. (a) Visible PL emission at 300 K from microscopic whiskers formed by RIE in chlorine plasma. The PL excitation used a 325 nm HeCd laser line (23 mW), (b) infrared band-to-band emission from Si whiskers at RT.

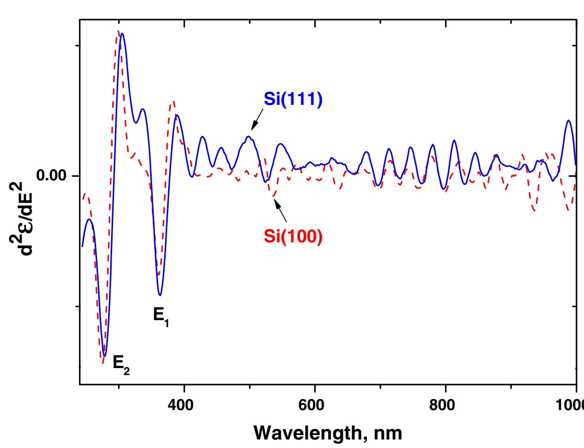

Fig. 3. Second derivative of the dielectric function **ε(E)** of Si whiskers indicating the observed critical points in the electronic band structure.

a characteristic PL in the visible region at 675 nm (2.23 eV) in Fig. 2a. The PL spectrum can be decomposed into three emission bands at 595, 645 and 695 nm. Visible emission features have been observed from the black Si formed by femtosecond laser pulses [8] and those produced in CF_4/O_2 plasma using Al_2O_3 cathode [4] and Si nanorods [9]. These features can be due to defects mediated recombination mechanisms [10].

The whiskers exhibit also an infrared PL near the band edge of the bulk Si which is attributable to band-to-band (BB) free carrier recombination. Fig. 2b compares the room temperature (RT) PL spectra of whiskers formed on Si (1 0 0) and Si (1 1 1) wafers. The emission intensity for those fabricated on Si (1 1 1) is much stronger probably due to their length and light harvesting efficiency. Similar observations were reported for epitaxial Si nanowires and the BB emission was attributed to spatial confinement effect [11]. However, the observation of the BB at 1.09 eV at 300 K from porous Si has been also reported and attributed to [12]. In both cases, the relaxation of selection rules at low dimensions can be the reason behind the direct transitions at the zone center [13].

SE analysis gives clues about the electronic band structure and dielectric properties of the Si whiskers. As shown in Fig. 3, the critical points E_1 at 3.43 eV and E_2 at 4.52 eV are very strong and their position depend on the whisker size. Figure compares the second derivative of the dielectric function for the whiskers grown on Si (1 0 0) and Si (1 1 1). When compared with Si (1 1 1), the E_1 and E_2 bands for whiskers in Si (1 0 0) are blue shifted by 28 and 82 meV, respectively. These shifts are attributable to the fact that the whiskers grown on Si (1 0 0) are much shorter than those grown on Si (1 1 1). The shorter whiskers can lead to further quantization due to length reduction. The whiskers on Si (1 0 0) are 35%

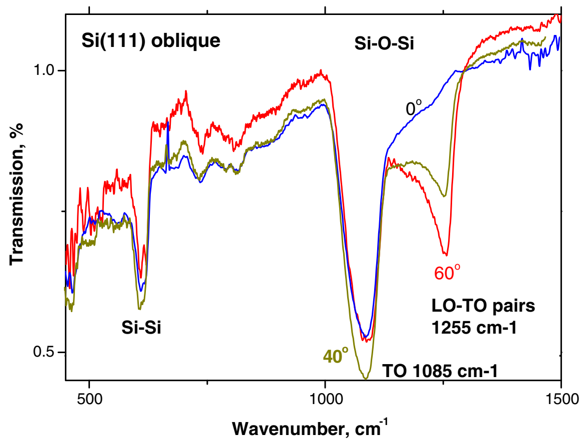

Fig. 4. Infrared spectrum of a Si whisker at oblique incidence indicating the importance of LO–TO disorder induced mode coupling.

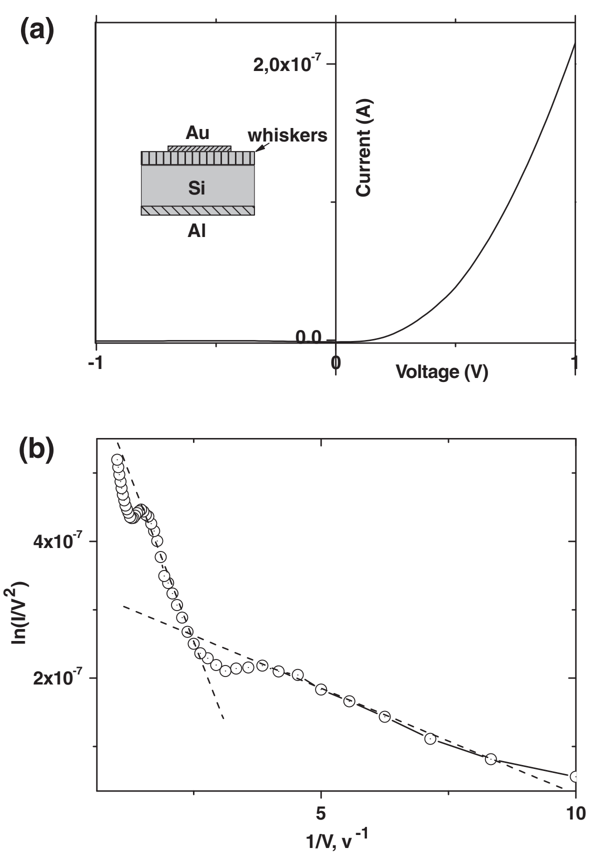

Fig. 5. Current–voltage characteristics of a silicon whisker diode as measured at room temperature. (a) *I–V* plot and (b) Fowler–Nordheim plot. A schematic of the device structure is inserted consisting of 200 nm back contact Al and 20 nm of Au front electrode. The distance between electrodes is about 200 μm and the active device area is around 0.03 cm^2.

shorter than those on Si (1 1 1) as evidenced from SEM and TEM analysis.

We show that coupled LO–TO vibrational modes of Si–O can be used in assessing the amount of strain and defects on the wafer. Fig. 4 supports the findings of EDS and TEM analysis through the Si–O–Si stretching vibrations at 1085 cm^{-1}. Note that the band at 1255 cm^{-1} can only be visible at oblique incidence (4° and 60°). This behavior could be interpreted as the disorder induced mode coupling of LO–TO modes [14]. The strength of this change can be used to assess the significance of defects. Similar changes have also been observed in acid vapor exposed Si nanorods [9]. However, they consist of acid vapor exposed Si nanorods having characteristic N–H and Si–H vibrations. The presence of a native oxide encapsulation around the pillars should be at the origin of such properties [14,15].

In order to determine the diode performance and validate the fabrication procedure, devices were fabricated on Si whiskers. Room temperature current–voltage (*I–V*) characteristics of such a device are shown in Fig. 5, indicating extremely low leakage current. Fig. 5 shows typical current–voltage characteristics (a) and the corresponding Fowler–Nordheim (F–N) plot [ln (IV^{-2}] versus V^{-1} of the same data (b). The straight F–N characteristics suggest field emission is occurring in the diode structure. Two slope F–N emission has already been reported [16] and as possible cause such as oxide layer or tip distribution is under investigation. A plateau between two slopes is a typical of a field emission from a p-type semiconductor where the field penetration creates a depletion region and causes the current to be limited by electrons and not by the transparency of the barrier [17]. The enhancement factor β can be estimated to be about 2000 using the following phenomenological formula [18].

$$\beta = 1 + s(d/r_o)$$

Where d and r_o are anode-to-cathode spacing and radius of curvature for whiskers, respectively. s is the screening effect parameters, whose range is between 0 for very dense whiskers and 1 for a single tip. Assuming densely arranged whiskers ($s = 0.2$) and $b_o = 10$ nm which are located in a parallel plate electrical field ($d = 200$ μm), $\beta = 2000$.

4. Conclusion

Si whiskers can have a significant impact on new technologies, particularly on the development of new solar cells, field emission cathodes and variety of nano-electronics devices [19]. Particularly, the possibility of fabricating broadband antireflective Si whiskers without the use of lithography offers an interesting low-cost process for optical component production. Physical properties of these whiskers can be controlled by a number of experimental variables. Disorder induced optical modes (LO–TO coupling) can be used as an effective tool in assessing optical/electronic quality of the whiskers.

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