

PROPERTIES OF NANOSTRUCTURED MATERIALS ASSISTED BY CAPILLARY-CELL METHOD

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Wafers of silicon and compound semiconductors were treated in a capillary-cell by using electrochemical or chemical etching (stain etching). Atomic force microscopy, infrared spectroscopy and Raman scattering methods revealed nanoporous and nanocrystalline structure of the treated surfaces. The formed porous semiconductors demonstrated efficient photoluminescence, which could be controlled by etching parameters, i.e. current density, electrolyte content, etc. These results indicate good prospects of the employed capillary-cell method for preparing nanostructured porous materials with desired structure and optical properties.

Introduction

The well-known method of electrochemical nanostructuring of materials allows us to form nanostructures of Si and compound semiconductors with desired sizes and morphology [1]. Since this method requires both a specially desired cell from chemically inert material and a good electrical contact to the treated substrates, it is hardly compatible with modern semiconductor technology. An alternative method of the chemical etching (stain etching process) is contactless but it is characterized by low reproducibility as well as by uncertainty of sizes and morphology of the formed nanostructures [2]. In the present work we have realized a simple configuration of the electrochemical etching cell, which employs the capillary effect in order to store the electrolyte between two or more working electrodes (semiconductor wafers). In this approach, the treated substrates (e.g. semiconductor wafers) are located in the capillary region and they can be etched by due to either the electrochemical (anodization) or chemical (stain etching) processes. The structure and optical properties of the obtained samples were analyzed by using atomic force microscopy (AFM), Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, and photoluminescence (PL) methods, which revealed nanoporous and nanocrystalline structure of the prepared materials.

Experimental

Figure 1 shows a scheme of the capillary-cell method in two simplest configurations. The two-electrode cell configuration (Fig.1, a) employs only two semiconductor wafers as the real working electrodes (anode and cathode). The back sides of the working electrodes were covered by metal contacts, e.g. by InGa alloy or Ag-paste. The multi-electrode cell method (Fig.1, b) consists of both the real working electrodes (semiconductor or metal wafers) and virtual electrodes, i.e. semiconductor wafers inserted between the working electrodes. Note, the electrolyte was kept between the working and virtual electrodes due to the capillary forces, which determine the maximal distance between electrodes. In our experiments, the thickness, L , of the capillary region between two opposite electrodes was controlled by inert spacers and it was typically of about 100-500 μm .

Samples of porous Si (por-Si) were formed from monocrystalline Si (c-Si) and multicrystalline Si (multi-Si) wafers of p-type with specific resistivity, ρ , of 1, 2, and 10 $\Omega\cdot\text{cm}$. The electrolyte for porous Si formation was based on mixtures of HF (48%) and ethanol ($\text{C}_2\text{H}_6\text{O}$), etoxyethanol ($\text{C}_4\text{H}_{10}\text{O}_2$) or acetonitrile ($\text{C}_2\text{H}_3\text{N}$). Samples of porous GaP (por-GaP) and porous GaAs (por-GaAs) were obtained by the electrochemical etching of the bulk n-(100) GaP:Te ($n=10^{17}\text{ cm}^{-3}$) and n-(100) GaAs:Te ($n=10^{18}\text{ cm}^{-3}$) in HF-based solutions. Typical lateral sizes of the treated wafers were $5\times 10\text{ mm}^2$. The samples were anodized during time, τ , of 1-40 minutes under etching current density, j , varied from 1 to 50 mA/cm^2 .

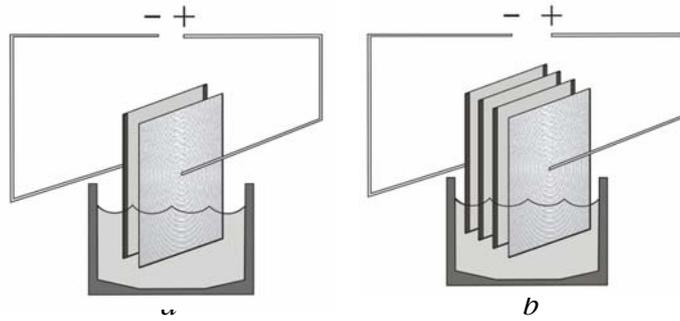


Fig.1. Schemes of the capillary-cell setup with two (a) and more (b) electrodes (wafers)

AFM study was carried out by using an Integra Therna microscope. Raman scattering measurements were made using a LabRAM HR 800 microRaman spectrometer equipped by an Ar-laser with wavelength of 488 nm for the excitation. A Bruker FTIR spectrometer was used for the transmittance and reflectance measurements in the spectral range from 300 to 7000 cm^{-1} . The PL was excited by a N_2 -laser (wavelength of 337 nm, pulse duration of 10 ns, repetition rate of 100 Hz). The PL signal was dispersed by a 50 cm monochromator and was detected by a CCD array in the spectral range from 400 to 1000 nm. The experiments were carried out in air at room temperature.

Results and Discussion

Typical AFM image of porous Si formed due to the electrochemical etching in the capillary-cell filled with $\text{HF}:\text{C}_2\text{H}_3\text{N}=1:1$ is shown in Figure 2. Both nano- and micro- structures are revealed in the AFM picture. The nanostructures (peaks and deeps) with height of the order of 10 nm and smaller are evidently formed due to the growth of nanopores [1]. Structures with sizes from 0.1 to 0.5 μm are probably formed because of the pore unification or/and release of the reaction products (hydrogen evolution) as well as due to self-organization processes on the treated surface. The FTIR study showed that the internal surface of porous Si layer formed by the capillary cell method was mostly covered by Si-H_x ($x=1,2,3$) and Si-O bonds. The characteristic vibrations of C-H and O-H surface groups were also observed in the FTIR spectra of porous Si, which indicated the presence of adsorbed molecules from electrolytes and air. In general, the FTIR spectra of porous Si formed in the capillary-cell were similar to that of the samples formed in the convenient electrochemical cell in the same electrolyte [3].

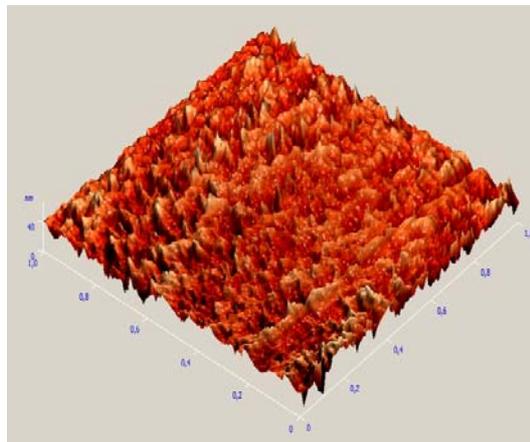


Fig. 2. Typical AFM image of a sample of porous Si formed by the capillary-cell method

Figure 3 shows typical spectra of the Raman scattering from c-Si and multi-Si substrates as well as the corresponding porous Si layers formed by the capillary-cell method. The Raman spectra

of porous Si consist mainly of one-phonon line at 516-519 cm^{-1} , which is shifted in respect to the Raman scattering line of Si-substrates (520 cm^{-1}) due to the quantum confinements for phonons in nearly spherical Si nanocrystals with sizes of 2-5 nm [4]. An enhancement of the Raman scattering intensity of porous Si can be explained by local electric-field effects in semiconductor structures with sizes larger than 10 nm [5].

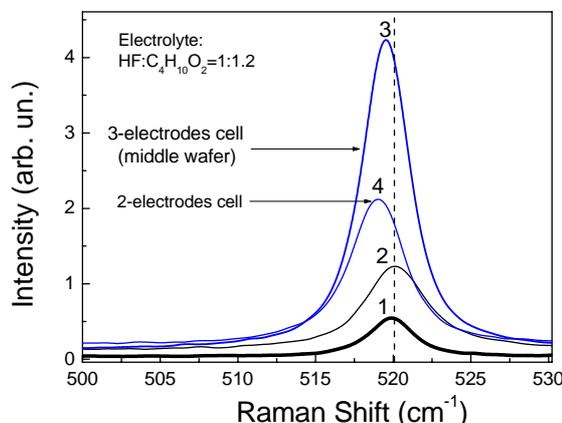


Fig. 3. Raman scattering spectra c-Si (1) and multi-Si (2) wafers and porous Si layers prepared from c-Si (3) and multi-Si (4) by the capillary method in 2- and 3-electrodes cells

Figure 4 shows spectra of the Raman scattering from c-GaP substrate and corresponding porous GaP layer formed by the capillary-cell method. Because of the used excitation geometry as well as the crystallographic orientation of the samples, the Raman spectra of c-GaP exhibit the scattering lines only of LO phonons with frequency $\omega = 403 \text{ cm}^{-1}$. However, the Raman spectra of por-GaP show the peaks both LO and TO vibrations at 403 cm^{-1} and 365 cm^{-1} , correspondingly. The appearance of the TO peak can be explained by the Raman scattering from the disoriented structural elements in nanostructures of por-GaP. Furthermore, the scattering at 395-397 cm^{-1} was also observed as a shoulder of the LO-line (see Fig.4). This shoulder can be explained by a contribution of the surface phonons in GaP nanocrystals with sizes of about 100 nm or less [6]. The contribution of surface phonons was also observed in Raman spectra of the prepared por-GaAs, which consist also of the Raman lines of LO and TO phonons as well as the vibration peaks attributed to oxidized surface regions similarly to the result reported for the por-GaAs formed in the conventional electrochemical cell [7].

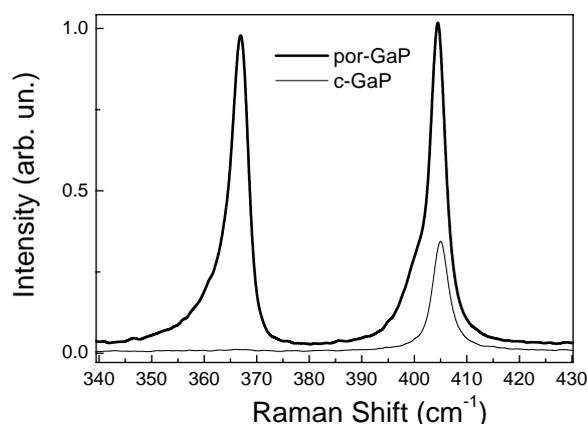


Fig. 4. Raman scattering spectra of c-GaP and porous GaP prepared by the capillary method (2-electrodes cell, HF:C₄H₁₀O₂=1:1.2, $j=5 \text{ mA/cm}^2$, $\tau=37 \text{ min}$)

Figure 5 and 6 show PL spectra of por-Si samples formed in the capillary-cell under different etching regimes and configurations. It should be noted, that the PL emission of por-Si in the range of 500-900 nm is usually attributed to the radiative recombination of excitons confined in Si nanocrystals with characteristic minimal sizes of about 1-5 nm [1,8]. The spectral position of PL line is determined by the quantum confinement effect and Coulomb interaction (exciton effect) [8]. Rather large broadening of the PL band can be explained by the size distribution in Si nanocrystal ensemble. It is known that the PL intensity of por-Si depends on passivation of Si nanocrystal surfaces [1,3]. As one can see from Fig.5 the PL intensity of por-Si formed by the capillary-cell method is maximal for the samples formed at low etching current density. Note that the nearly constant flowed charge was kept for the investigated samples.

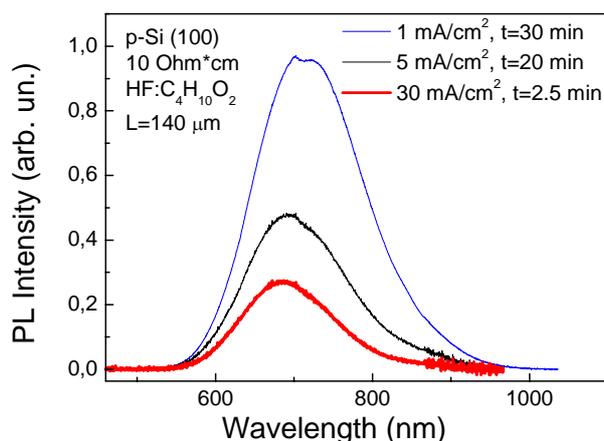


Fig. 5. Photoluminescence spectra of porous Si prepared from (100) p-Si ($\rho=10 \Omega\text{-cm}$) at different etching current densities and duration in the capillary cell with $L=140 \mu\text{m}$

This effect can be explained by taking into account the limited amount of electrolyte and space for the hydrogen evolution in the employed capillary cell. Thus, the relatively slow etching rates are preferable for the capillary-cell method in comparison to the conventional macroscopic-cell approach [1,3].

Figure 6 demonstrates that the PL intensity of por-Si formed by the capillary-cell method with L in the range from 100 to 500 μm does not strongly depend on L . However, the PL properties can be controlled by etching parameters (electrolyte content, etching duration, current density etc.) and substrate characteristics. The samples of brightly luminescent por-Si were formed from both c-Si and multi-Si wafers in the capillary-cell method. Furthermore, we used the capillary-cell method in order to prepare luminescent por-Si layers under the stain etching process (see Fig.6). On the one hand, the spectral position and intensity of PL bands of the samples prepared by the capillary-cell method were similar to that for the conventional por-Si formed by electrochemical or chemical etching [1,2]. On the other hand, the luminescent Si nanostructures formed by the capillary-cell method require rather limited amount of the electrolyte as well as they can be easily prepared without electrical contacts and bias voltage. The later properties are obviously important for applications in scalable technology for the formation of semiconductor nanostructures.

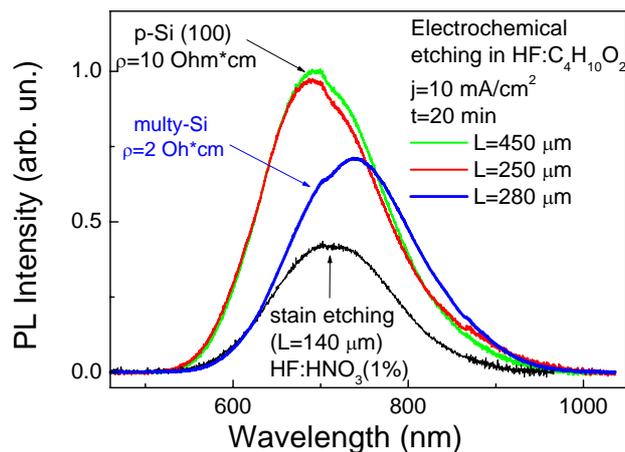


Fig. 6. Photoluminescence spectra of porous Si prepared from c-Si and multi-Si of p-type wafers by chemical (stain etching) or electrochemical etching at different thickness of capillary layer

Conclusions

The capillary-method was used to prepare nanostructures semiconductor materials from bulk Si, GaP, and GaAs. The obtained porous layers exhibit optical properties of semiconductor nanostructures with sizes in the range from 1 to 100 nm. The PL study of the formed porous Si layers demonstrated possibilities to control their parameters (intensity and spectral position) by changing the etching conditions (current density, electrolyte content), however the thickness of the capillary region did not effect significantly the photoluminescence properties of the investigated samples. The obtained results showed that the capillary method could be perspective for applications in both laboratories and industry conditions to prepare nanostructured materials with desired structure and optical properties.

References

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КАПИЛЛЯРЛЫҚ ӘДІСПЕН ДАЙЫНДАЛҒАН НАНОҚҰРЫЛЫМДЫ МАТЕРИАЛДАРДЫҢ ҚАСИЕТТЕРІ

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Кремний және құрамды жартылай өткізгіштерден жасалған төсеніштер капиллярлық ұяшықтарда электрохимиялық және химиялық уландыруды қолданып уландырылған (түсті уландыру). Атомдық-күш микроскопиясы, ИҚ спектроскопиясы және Раман шашыраудың көмегімен уландырылған беттерінің нанокеукті және нанокристалдық құрылысы белгіленген. Қалыптастырылған кеукті жартылай өткізгіштер тиімді фотолюминесценцияны көрсетті, оны уландыру параметрлер бойынша бақылауға болады: анодтау тогының тығыздығы бойынша, электролиттің құрамы бойынша және т.б. Осы нәтижелер капиллярлық әдісті керекті құрылымы және оптикалық қасиеттері бар нанокұрылымды кеукті материалдарды жасауға өте жақсы мүмкіншілікті береді.

СВОЙСТВА НАНОСТРУКТУРИРОВАННЫХ МАТЕРИАЛОВ ПРИГОТОВЛЕННЫХ КАПИЛЛЯРНЫМ МЕТОДОМ

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Подложки из кремниевых и составных полупроводников были протравлены в капиллярной ячейке с использованием электрохимического и химического травления (окрашивающее травление). С помощью Атомно-силовой микроскопии, ИК спектроскопии и Рамановского рассеяния были выявлены как нанопористая, так и нанокристаллическая структуры протравленных поверхностей. Сформированные пористые полупроводники показали эффективную фотолюминесценцию, которая может контролироваться за счёт параметров травления, а именно плотности тока анодирования, состава электролита и так далее. Эти результаты дают хорошую перспективу использования капиллярного метода для изготовления наноструктурированных пористых материалов с желанными структурой и оптическими свойствами.