

Photoconductivity of Germanium Nanowire Arrays Incorporated in Anodic Aluminum Oxide

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Abstract. Photoconductivity of germanium nanowire arrays of 50 and 100 nm diameter incorporated into Anodic Aluminum Oxide (AAO) membranes illuminated with visible light is investigated. Photocurrent response to excitation radiation with time constants faster than 10^{-4} s were governed by absorption of incident light by nanowires, while photokinetics with time constants of the order of 10^{-3} s originates from the photoluminescence of the AAO matrix. Possible applications of nanowire arrays inside AAO as photoresistors are discussed.

1. Introduction

Nanometer-scale semiconductor technology is being gradually introduced in the production of novel electronic and optoelectronic devices [1,2]. Application of nanostructures such as high-density semiconductor nanowire arrays is a challenging task due to difficulties of contacting and addressing individual nanowires in the array. The synthesis of nanowires inside AAO pores provides well-ordered arrays of highly packed and oriented nanowires. Such three-dimensional (3D) materials have a huge potential in electronic applications. In particular, the problem of contacting the nanowires can be approached and solved in different ways, e.g., AAO membranes, similar to those used in this study, have recently been synthesized on silicon substrates [3,4], which is very promising for device integration using conventional semiconductor technology.

To date, the majority of works related to the optoelectronic properties of individual nanowires have been performed on direct band-gap materials such as InP [5], ZnO [6], SnO₂ [7], CdSe [8] and GaN [9]. Optical studies on elemental semiconductor (Si and Ge) nanowires have focused primarily on the confinement effects using photoluminescence measurements [10,11]. Only recently, Park et al. reported photoconductivity measurements on indirect gap semiconducting nanowire by performing optical scanning measurements on photocurrent in individual Si nanowire FETs [12]. Our recent studies demonstrate the first data about photoconductivity of Ge nanowire arrays inside AAO membranes [13].

In this work we present our studies on photoconductivity and photoluminescence of 50 and 100 nm germanium nanowire arrays inside AAO membranes. Germanium is a well-known semiconductor with an indirect band gap, E_g , of about 0.66 eV at room temperature [14]. Until now it has been widely used for fabrication of photodetectors [15-17], far-infrared photoresistors [18] and various other devices [19]. Contacting and conductivity characterization methods of Ge nanowires incorporated

inside AAO matrix are developed [20,21]. Here we address the optoelectronic properties of germanium in form of nanowire arrays incorporated in AAO, which is important for understanding its potential in optoelectronic devices.

2. Experimental

Ge nanowires were synthesized within the pores of a 40-60 μm thick AAO membranes using the supercritical fluid method [22]. The surface of the Ge filled AAO membrane was mechanically polished with diamond suspensions to remove the Ge layer overgrown on the membrane surfaces after the supercritical inclusion process. To expose the tops of the Ge nanowires above the membrane surface AAO had been etched back by approximately 100 nm, with 9 wt% phosphoric acid. Etching times between 15-45 and 3-10 minutes were used for Ge nanowire-AAO samples with mean nanowire diameters of 100 and 50 nm respectively [13]. The density of Ge nanowires within the AAO membranes was $9 \times 10^8 \text{ cm}^{-2}$ and $1.4 \times 10^{10} \text{ cm}^{-2}$ for mean pore diameters of 100 and 50 nm respectively.

To perform photoconductivity measurements, the top surface of the AAO membranes was coated with a semitransparent Au coating ($d \sim 25 \text{ nm}$). Meanwhile, a non-transparent ($d \sim 100 \text{ nm}$) Au electrode, 1 mm in diameter, was used as a bottom electrode. The top and bottom Au coatings were deposited in vacuum ($P \sim 10^{-6} \text{ Torr}$) at a deposition rate of about 1.7 \AA s^{-1} using a precision etching coating system (Gatan). To remove surface contamination and possible oxide layers from surface of nanowires before Au deposition, the samples were cleaned for 15 s using Ar ions with energy of 5 keV.

The sample was illuminated by a 100 mW Melles Griot multiline Ar laser ($\lambda = 457 - 514 \text{ nm}$). Continuous laser light was controlled by a photographic camera shutter (Nikon F80). Current passing through the samples was measured at a room temperature using a low-noise current amplifier SR570 (Stanford Research Systems) and recorded by a digital oscilloscope (Tektronix TDS1001).

Photoluminescence was excited by 350 nm Ar ion laser and spectra measured using home-made spectrophotometer. Light absorption was measured using an infrared spectrophotometer (Bruker Equinox 55).

3. Results

Individual Ge nanowires inside AAO membrane were probed in topography and conductivity measurements using conductive AFM (see figure 1a) as previously reported [20,21]. Figure 1b shows the current map of the Ge nanowire array surface with a mean diameter of 100 nm at applied voltage 15 V. The white spots indicate a current flow through the nanowires, while the dark background reflects the dielectric properties of the AAO matrix. The figure demonstrates that all pores were filled with Ge nanowires throughout the membrane.

Figure 2 a shows a typical dark current-voltage ($I(V)$) curve at room temperature for the Ge nanowire arrays. An increase in the current was observed for the samples upon illumination with an Ar laser, at an intensity of 800 mW cm^{-2} . Figure 2b shows the photocurrent (I_{ph}), $I_{\text{ph}} = I_t - I_d$, where I_d and I_t are the dark current and total current respectively, as a function of applied voltage for the Ge nanowire sample (pulse duration 0.5 ms). No photocurrent was detected in the empty AAO membranes, i.e. those not filled with Ge nanowires.

The nanowire photocurrent kinetics is shown in figure 3a. The estimated time constants were found to vary slightly with the nanowire diameter (table 1). The kinetics consists of two components (Figure 3a inset and Table 1). The first kinetic time constant (τ_1) is shorter than 10^{-4} s and therefore can not be determined by the 0.5 ms pulse used in the experiment. The time constant of the second kinetic component (τ_2) is in the range of 10^{-3} s . The first kinetic component can be attributed to the photo processes in the Ge nanowires. For comparison, the lifetime of charge carriers in polycrystalline bulk Ge is of the order of $3 \times 10^{-6} \text{ s}$ [23].

Table 1. Characteristic time constants for Ge nanowire-AAO samples.

Nanowire Diameter	τ_1 (ms)	τ_2 (ms)	
		increase	decrease
50 nm	< 0.1	0.4-4	3-7
100 nm	< 0.1	0.4-0.8	0.5-4

The second kinetic component (τ_2) may be associated with the presence of different charge traps in the GeNW-AAO system or photoprocesses inside AAO membrane. The light absorption and the photoluminescence of empty and filled AAO membranes were investigated in order to determine the impact of AAO matrix on the photoconductivity of Ge nanowires.

Light absorption in AAO membranes significantly increases at energies above 1.8 eV (figure 4a). The photoluminescence of AAO exhibited wide luminescence with the maximum of 2.8 eV (figure 4b, curve 1). The photoluminescence time constant (τ_{lum}) in the AAO matrix was measured to be in range 0.8-2.0 ms, which is close to the Ge nanowire array photoconductivity decay constant τ_2 . Based on this similarity we assign the photocurrent response with τ_2 in nanowires to the secondary photons produced in photoluminescence of the AAO as shown in figure 3b. Moreover, the intensity of the photoluminescence decreases significantly after filling the AAO pores with Ge nanowires (figure 4b, curve 2). The decrease of the photoluminescence intensity in nanowire matrix may be caused, firstly, by nanowires absorbing the primary light and thus decreasing its intensity and secondly, by nanowires absorbing part of the photoluminescent light from AAO matrix and consequently decreasing photoluminescence intensity (see figure 4b). Results show that it is important to take into account the influence of AAO photoluminescence on the photoconductivity processes when nanowire arrays will be used in fast optoelectronic devices for photodetection of light with wavelengths below 700 nm.

Bearing in mind the photocurrent values shown in figures 2b and the nanowire densities; we estimate that for the semi-transparent Au electrode the photocurrent in a single Ge nanowire, at a bias of 50 V and illumination power of 800 mW cm⁻², is in the range of 0.3 pA and 0.03 pA for mean diameters of 100 nm and 50 nm respectively. This indicates that individual Ge nanowire within AAO templates demonstrate a sufficient photo-induced current effect that can be used optoelectronic devices. The high density of the nanowire arrays may lead to design of optical imaging sensors with lateral resolution oversampling.

3. Conclusions

In conclusion, photo-induced conductivity in Ge nanowire arrays, with mean nanowire diameters of 50 and 100 nm, was demonstrated and impact of AAO matrix was analyzed. The Ge nanowire photoresistor arrays can be used in the detection of high intensity illumination. However, if the photoconductivity of Ge nanowires could be increased, e.g., by doping, the arrays could be used in the detection of low intensity and far infrared illumination.

4. Acknowledgments

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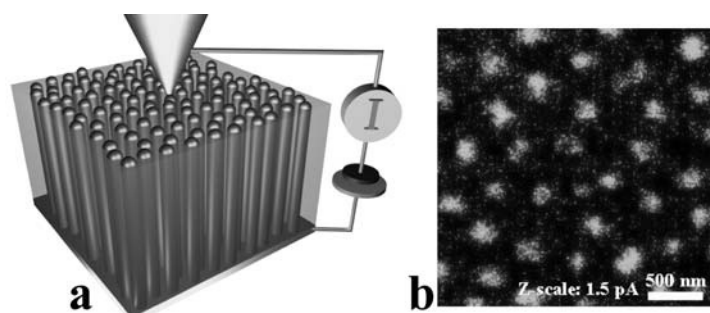


Figure 1. (a) Schematics of C-AFM electric probing of Ge nanowires inside AAO membrane. (b) - current map measured at 15 V on arrays of Ge nanowires (mean nanowire diameter of 100 nm).

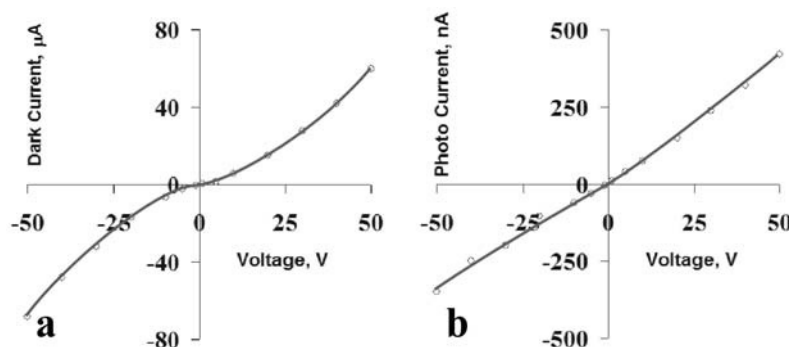


Figure 2. I(V) characteristics of Ge nanowire-AAO samples with a mean diameter of 100 nm: (a) dark currents from semi-transparent Au top electrodes, (b) photocurrents (I_{ph}) obtained using a laser intensity of 800 mW cm^{-2} measured after a 0.5 ms illumination.

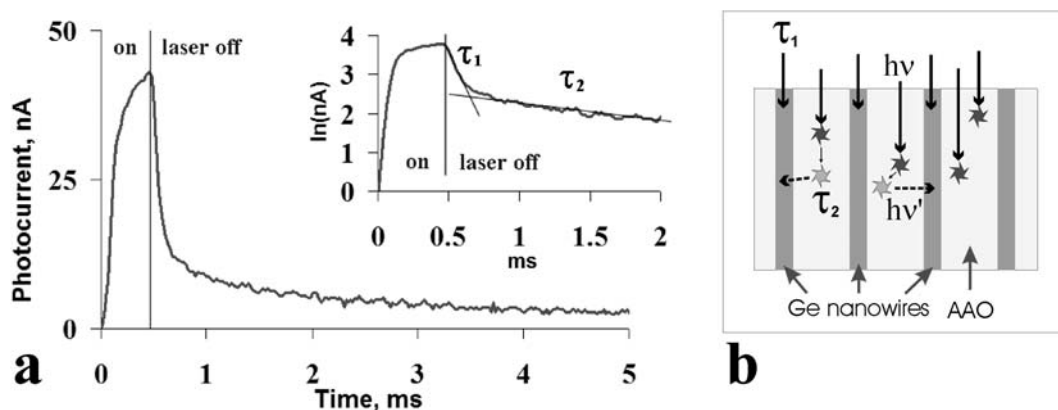


Figure 3 (a) Current response during 0.5 ms illumination by laser intensity 800 mW cm^{-2} for 100 nm nanowires with Au electrodes (kinetics of 50 nm nanowires is similar). Insert – photocurrent decay kinetics in semilogarithmic coordinates. (b): Scheme of light absorption in GeNW-AAO system. Laser photons (continuous arrows) directly absorbed by Ge nanowires create electron-hole pairs (recombination time constant τ_1). Photons may also be absorbed by AAO and they excite photoluminescence centers (dark stars), which relax to the normal state (time constant τ_{lum}) (gray stars) and emit accumulated energy as luminescence photons (dashed arrows). Then luminescent light may be absorbed by Ge nanowires and impact into photocurrent with time constant $\tau_2 = \tau_{\text{lum}}$.

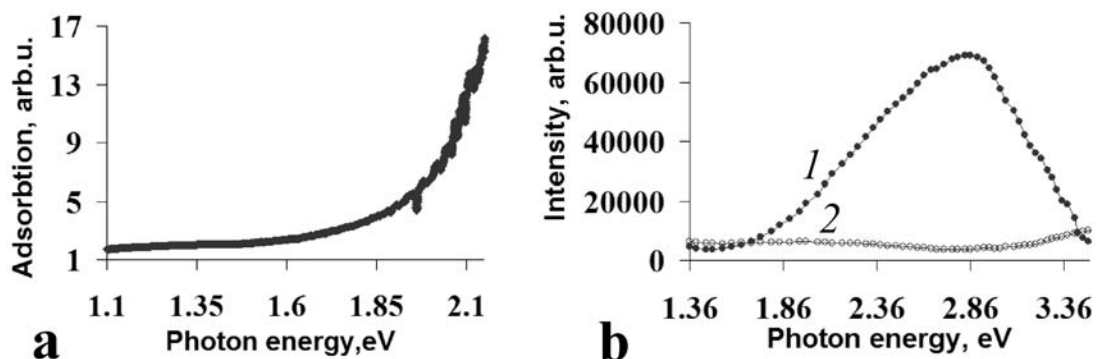


Figure 4. (a)– light absorption spectrum for empty 50 nm AAO membrane, (b) - photoluminescence of empty 50 nm AAO membrane (curve 1) and Ge filled AAO membrane (curve 2).