Thin Solid Films 613 (2016) 59–63

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

# A room temperature light source based on silicon nanowires

M.J. Lo Faro [a,b,c], C. D'Andrea [b], E. Messina [a], B. Fazio [a], P. Musumeci [c], G. Franzò [b], P.G. Gucciardi [a], C. Vasi [a], F. Priolo [b,c,d], F. Iacona [b], A. Irrera [a,*]

[a] CNR-IPCF, Istituto per i Processi Chimico-Fisici, V. le F. Stagno D'Alcontres 37, 98158 Messina, Italy
[b] MATIS CNR-IMM, Istituto per la Microelettronica e Microsistemi, Via Santa Sofia 64, 95123 Catania, Italy
[c] Dipartimento di Fisica e Astronomia, Università di Catania, Via Santa Sofia 64, 95123 Catania, Italy
[d] Scuola Superiore di Catania, Via Valdisavoia 9, 95123 Catania, Italy

ARTICLE INFO

*Article history:*
Received 6 July 2015
Received in revised form 6 November 2015
Accepted 10 November 2015
Available online 12 November 2015

*Keywords:*
Silicon
Silicon nanowires
Carbon nanotubes
Metal assisted chemical etching
Room temperature photoluminescence
Multiwavelength light source

ABSTRACT

We synthesized ultrathin Si nanowires (NWs) by metal assisted chemical wet etching, using a very thin discontinuous Au layer as precursor for the process. A bright room temperature emission in the visible range due to electron–hole recombination in quantum confined Si NWs is reported. A single walled carbon nanotube (CNT) suspension was prepared and dispersed in Si NW samples. The hybrid Si NW/CNT system exhibits a double emission at room temperature, both in the visible (due to Si NWs) and the IR (due to CNTs) range, thus demonstrating the realization of a low-cost material with promising perspectives for applications in Si-based photonics.



## 1. Introduction

Silicon is the most widely used material in microelectronics and photovoltaics, due its availability, cheapness, well-established and scalable technology. Despite these features, its implementation as photon emitter in light sources is still a very problematic issue, since it is an indirect band-gap material and light emission hardly occurs, limiting applications in photonic devices.

Si nanowires (NWs) are considered one of the most promising nanomaterials due to their unique characteristics of electrical and thermal conductivity, to their optical properties and for their compatibility with Si-based technology. Si NWs are already widely used for several applications, including photovoltaics [1], microelectronics [2], and sensing [3], but there is a substantial lack of photonic applications. Si NWs are commonly synthesized by techniques exploiting the vapor–liquid–solid (VLS) mechanism [4–6]. VLS processes are based on thermodynamic properties of metal–Si alloys and generally use Au as catalyst due to the low Au–Si eutectic temperature. The temperature-induced Au diffusion detrimentally affects Si electrical and optical properties, introducing deep energy levels responsible for non-radiative phenomena [7]. Furthermore, in situ doping of Si NWs is not uniformly controlled since it is highly affected by the dopant segregation at the wire surface [8]. Finally, VLS processes do not allow to obtain Si NWs with radii lower than a critical values of tens of nanometers, far beyond the quantum confinement threshold [9]; the latter limitation holds also for wires synthesized by top-down lithographic processes. In agreement with the above considerations, the observation of photoluminescence (PL) from Si NWs has been attributed to the presence of N-containing complexes [10] or to the phonon-assisted low temperature recombination of photogenerated carriers [11]. PL from Si NWs due to quantum confinement has been only obtained by reducing, through thermal oxidation processes, the diameter of NWs obtained by plasma etching of a Si wafer [12,13], or by a $TiSi_2$-catalyzed VLS growth [14].

Metal assisted wet etching processes are a promising alternative method for Si NW synthesis [15–18]. In such an approach, the metal catalyst is usually added to the etching solution as a salt (typically $AgNO_3$). However, the use of salts leads to the formation of dendrites, whose subsequent removal could damage the NWs [15,18]. Note also that NWs with mean radius smaller than 30 nm have been never obtained by etching processes assisted by metal salts [18].

We previously demonstrated the realization of room temperature light emitting Si NWs by using an easy and controllable approach: the metal assisted chemical etching catalyzed by a thin Au layer [19]. In this process, any Au contamination is prevented since each step of the synthesis is performed at room temperature and the catalyst is easily and fully removable by a proper chemical etching. The proposed method is a cheap and maskless process for the synthesis of vertically aligned high density array of NWs that guarantees a high control of

* Corresponding author.
*E-mail address:* irrera@me.cnr.it (A. Irrera).

http://dx.doi.org/10.1016/j.tsf.2015.11.028
0040-6090/

the structural and optical features [19]. Particularly remarkable is the possibility to obtain NWs with ultrathin diameters smaller than 10 nm, which exhibit an intense and size-dependent visible emission at room temperature, in agreement with quantum confinement theory.

In this work, we report the realization of a hybrid system obtained combining light emitting Si NWs and single walled carbon nanotubes (CNTs), which are attracting the interest of scientific community due to their remarkable optical [20–22] and electrical properties [23]. The Si NW/CNT system is a low-cost material that emits at room temperature both visible and IR photons, with the possibility to tune the emission wavelength in both spectral ranges. The obtained results are extremely promising and may open new perspectives in Si photonics. In particular, IR emission is strategic for telecommunication applications. The synthesis of a Si-based material that emits at wavelengths close to the region of minimum loss of $SiO_2$ optical fibers is a very challenging task; different approaches, mainly based on Er-doping, have been followed to achieve this result [24–27]. In this framework, the Si NW/CNT system we are proposing guarantees a full compatibility with Si technology at low-cost and exhibits, as a unique feature, the possibility to tune the IR emission by varying CNT chirality.

## 2. Experimental details

Si NWs were obtained from p-type (100) oriented Si wafers, with resistivity of 1–5 Ω·cm, corresponding to a B concentration of $10^{16}$ $cm^{-3}$. Wafers were cut in small pieces that were UV-oxidized for 2 min and then dipped in a 5% aqueous solution of HF for 5 min, in order to have an oxide-free substrate. Then we deposited 2 nm of Au by using room temperature electron beam evaporation of high purity pellets (99.99%), realizing a discontinuous layer. We performed a room temperature etching of the Au-covered samples in an aqueous solution of HF (5 M) and $H_2O_2$ (0.44 M) to synthesize Si NWs. During the etching, due to the difference of electronegativity at the Au/Si interface, Au draws electrons from Si, so that a $SiO_2$ layer is selectively formed only underneath the metal covered regions and then removed by HF [19]. Finally, the Au layer used for the process is removed via chemical etching in a KI + $I_2$ aqueous solution.

A CNT dispersion was obtained by using commercially available single walled CNT powder enriched in chiralities (7,5) and (7,6) from SouthWest NanoTechnologies Inc. To avoid bundle formation [28,29], 2 mg of CNTs were added to 10 ml of deionized water with 0.2 g of sodium taurodeoxycholic acid as surfactant, and then treated for 30 min in a sonicator bath. Precipitates and carbonaceous residues were removed by ultracentrifugation using an Optima Max-XP tabletop ultracentrifuge, equipped with a swinging bucket rotor MLS-50, operating at 45,000 rpm for 45 min. We realized a Si NW/CNT hybrid system by cutting NW samples in pieces of 0.5 × 1 $cm^2$ and then dropcasting 5 μl of CNT dispersion on the top.

Structural characterization was performed by using scanning electron microscopy (SEM) with a field emission Zeiss Supra 25 microscope. Room temperature PL measurements were obtained by exciting the system with the 364 nm line of an $Ar^+$ laser, focused through a fluorinated 60× (NA = 0.9) Olympus objective and with the 633 nm line of a He–Ne laser, operating with a 100× (NA = 0.9) objective. Room temperature PL spectra were acquired by HR800 spectrometer (Horiba Jobin-Yvon), equipped with a CCD (Synapse) Peltier-cooled detector for visible detection and with an InGaAs array (Symphony II) $N_2$-cooled detector for IR detection. PL lifetime measurements were performed by optically pumping the system to the steady state with the 488 nm line of an $Ar^+$ laser and then monitoring the decay time of the PL signal with a water-cooled photomultiplier tube. The incident laser beam was chopped by an acousto-optic modulator at a frequency of 55 Hz and the overall time resolution of the detection system is 200 ns.

## 3. Results and discussion

### 3.1. Structural characterization

In Fig. 1, a cross-section view SEM image of a Si NW template obtained after the metal assisted etching is reported. This method easily allows to vary the length of Si NWs by changing the etching time; in the case of the displayed SEM image, we obtained 2.6 μm long NWs by using an etching time of 8 min, but NW length dependence on the etching time is strongly affected by the doping level of the substrate [30]. As visible from the image, a very dense array of uniformly vertically aligned Si NWs is achieved; typical density values are $10^{11}$ NWs/$cm^2$, corresponding approximately to a 50% NW coverage of the total exposed area. The great potentiality of this method is related to the accurate control of the NW structural features. As reported in our previous work, we can vary NW diameter on the nanometric scale by changing the thickness of the metallic layer or the nature of the metal precursor [31]. Moreover, with this approach we can achieve NWs with the same doping of the starting Si substrate, that is a fundamental prerequisite for device fabrication. Si NWs shown in Fig. 1 have an ultrathin diameter of about 7 nm, as determined by Raman spectroscopy and transmission electron microscopy [31–34], that is a suitable size for the occurrence of quantum confinement.

### 3.2. Optical characterization

Fig. 2(a) displays the room temperature PL spectra of Si NWs having same the diameter of 7 nm but different lengths, ranging from 1 to 3.5 μm. All peaks are due to electron–hole recombination in confined Si NWs and consist of a broad band with FWHM of about 160 nm, related to NW size distribution determined by the morphology of the thin Au layer. The emission spectrum is peaked at about 690 nm for NWs with size of 7 nm, but we have already demonstrated that it is possible to tune the emission wavelength by controlling the size of NWs in good agreement with quantum confinement theory [31]. The figure demonstrates that longer NWs have a more intense emission and this is due to the fact that in a single wire a huge ensemble of emitting centers is present, so the longer is the NW the more electron–hole pairs are present [34].

The inset in the left upper corner of Fig. 2(a) displays a photo of the emission of 2 μm long Si NWs, obtained by defocusing the 364 nm line of $Ar^+$ laser on the sample, showing that the very bright red emission is clearly observable by the naked eyes.

The lifetime of the system was measured by analyzing the time decay of the PL signal after the laser shut-off and by fitting the curve with an exponential function, as reported in Fig. 2(b), obtaining a value of 25 μs.

Another important peculiarity is that in this material non-radiative phenomena are not efficient [32]. Since NWs are an almost 1D system, radiative recombination may occur in points of the wire that are very

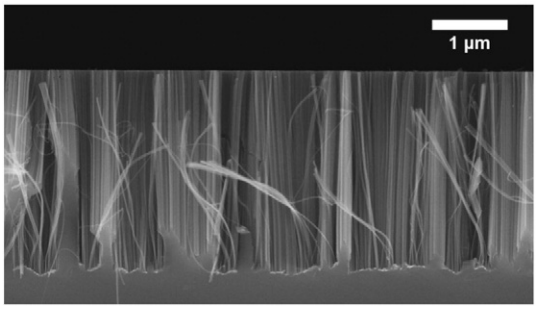


**Fig. 1.** Cross-section SEM image of Si NWs obtained by metal assisted chemical etching, displaying a dense template of vertically aligned 2.6 μm long wires.