Photoluminescence Emission from a nanofabricated Scanning Probe Tip Made of Epitaxial Germanium

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Keywords: scanning probe tip, photoluminescence, nano-optics, focused ion beam

Abstract We discuss a new type of nanoscale photon source constituted by a micro-pyramid made of epitaxial semiconductor material (Ge) attached to a silicon cantilever optimized for Atomic Force Microscopy and shaped by means of low-current Focused Ion Beam (FIB) milling. The optical characterization of these tips demonstrates sizeable photoluminescence emission at the direct energy gap of Ge (1550 nm). We have checked by independent measurements on the nano-patterned epitaxial material prior to the tip shaping process that the photoluminescence yield is not significantly affected by FIB milling, indicating that the optical properties of the material in this wavelength range are preserved. We envisage an application of this tool as a scanning probe in apertureless scanning near-field optical microscopy.

High-resolution optical imaging has become a fundamental tool in nanoscience and nanotechnology and is playing a key role in physical sciences, biology, medicine and telecommunications. The majority of far-field optical microscopy techniques are extensively used for imaging biological samples, but they hardly overcome light diffraction, setting a limit to the lateral resolution that is slightly below the optical wavelength λ (0.4 to 1.5 μm including the near-infrared range). This fundamental limit, recently overcome in the optical far-field by super-resolution microscopy techniques [1,2,3,4,5], was first surpassed by means of Scanning Near-field Optical Microscopy (SNOM) [6]. This peculiar microscopy approach, performed by scanning a nanoscale probe at a distance from the sample much smaller than λ , is the only technique that allows imaging with a lateral resolution that does not depend on the wavelength, but rather on the size of the probe itself. The photon source, scanned in close proximity to the sample surface by piezo-stages borrowed from atomic force microscopy (AFM) technology, can be constituted by an aperture at the apex of a tapered fiber or hollow-pyramid probe (aperture-SNOM) or by a sharp tip that can either scatter the near fields of the samples or act as a nanoscale light source (scattering-SNOM or apertureless-SNOM). SNOM systems typically attain lateral resolutions of the order of 10 to 100 nm depending on the probe geometry, probe-sample distance, and type of electromagnetic coupling with the sample. This is why the core of the SNOM system is the scanning probe tip that, if properly tailored from an accurately chosen material, has the capability to enhance the performances and widen the possible applications of this technique.

In this work, we summarize the fabrication procedure and describe the optical characterization of a new type of scanning nanoscale photon source for apertureless-SNOM applications. The source is constituted by a micro-pyramid made of epitaxial semiconductor material (Ge), attached to a silicon cantilever optimized for AFM. The micro-pyramid acts as an effective probe emitting, under optical excitation, photoluminescence (PL) photons at the direct energy-gap E_g of the semiconductor.

One-photon PL emission in semiconductors can be related to fluorescence in organic dye molecules or color centers, because in both phenomena an external laser source with wavelength $\lambda_0 < \lambda$ is needed to obtain photon emission at λ . Many nanoscale fluorescent

scanning probes [7] have been developed in the last years, with possible applications in biology [8,9] or in quantum telecommunications [10,11]. Only in few cases, PL from a semiconductor has been exploited for apertureless-SNOM: for example, in Ref. [8] CdSe nanocrystals emitting at $\lambda \approx 600$ nm have been used for fluorescence resonance energy transfer (FRET) imaging, a very popular technique to determine molecular scale distances in biological samples. Semiconductors display several advantages over fluorescent organic dye molecules and color centers: their band structure (hence the value of $E_g = \hbar c / \lambda$) can be readily tailored via control of size, composition and shape of the emitter so to provide broad spectral coverage with symmetric emission line profiles; due to their continuous absorption band at energies above E_g , they can be excited efficiently at $\lambda_0 \ll \lambda$ thereby reducing direct acceptor excitation and hence donor-acceptor cross-talk; finally, semiconductors are more stable emitters if compared to dye molecules.

In previous experiments, bottom-up approaches were followed to fabricate apertureless SNOM probes: in Refs. [8] and [12] CdSe semiconductor nanocrystals were linked to existing pyramidal tips for AFM by coating them with organosilane molecules, and in Ref. [13] fluorescent oxide nanoparticles were deposited directly on a tapered fiber tip placed in the deposition chamber. Here instead we follow a top-down fabrication approach, starting from high-quality epitaxial semiconductor material grown on a wafer. The epitaxial material layer is first patterned into micro-pillars and then the pillar shape is modified by focused ion beam (FIB) milling and electron-beam induced deposition (EB-ID), both performed in the vacuum chamber of a Zeiss Crossbeam apparatus [14]. Here we used germanium ($E_g = 0.80$ eV) as the epitaxial material and we detected the PL emission from the fabricated tip at $\lambda = 1550$ nm, which is the standard telecom wavelength of long-haul fiber-optic networks. Germanium epitaxially grown on silicon wafers (Ge/Si) is widely used as a detector in integrated silicon photonics chips. Also, the emission properties of Ge/Si are being investigated with the aim of obtaining laser emission from devices integrated on silicon chips. It is therefore expected that Ge/Si epitaxial wafers may become an important material for future optoelectronic applications [15,16,17,18,19].

Figure 1. Fabrication and imaging of the scanning probe with epitaxial Ge tip. (a) The visible-apex of the cantilever with a raw block of epitaxial germanium glued to its flattened apex. (b) The pyramidal tip after fabrication by focused ion beam. (c) Elastic scattering imaging of the tip performed in the

confocal setup with the excitation laser at 785 nm used for PL excitation. (d) A cartoon of the fabricated probe.

Fabrication

The technique for attaching epitaxial semiconductor layers grown on a wafer to the flattened apex of an AFM cantilever is described in details in Ref. [14]. Briefly, the epitaxial layers are first etched into micro-pillars (height 6-8 μm , diameter 1-2 μm) by dry etching techniques. Then, the AFM cantilever apex is placed in contact with the pillar surface and attached to it via EB-ID. This is a typical process obtained by the decomposing gaseous molecules, in our case by a carbon-platinum alloy, using an electron beam that leads to the deposition of non-volatile fragments onto a nearby cantilever. The deposition rate was about 10 nm/s and the whole scanning deposition has been computer controlled. Subsequently, the pillar base is cut by FIB milling and the epitaxial layer block is lifted out of the wafer by the AFM cantilever itself.

To sculpture the raw material block attached to the silicon cantilever into a pyramidal tip for SNOM applications we use low-current FIB milling. This technique allows avoiding the direct exposition of the internal part of the block to chemical etching or physical milling agents. Also, an excessive mechanical and radiation stress is avoided, which allows preserving the high crystal quality typical of the epitaxial layers. The AFM cantilever chip with the raw material block attached to the apex (Fig. 1a) is mounted on an especially-developed holder that allows one to remotely tilt and rotate the chip with high precision and minimal drift. The material block is imaged by SEM and the corresponding milling pattern for FIB is calculated by taking into account the angle between the electron and the ion column. The milling pattern includes tilt and rotation steps of the holder as appropriate to produce the final structure. We produce tips in the shape of four-sided pyramids with different apical angle (30 to 70 degrees), axis length (0.8 to 2 μm) and radius of curvature at the apex (30 to 100 nm). One example is shown in Fig. 1b. The fabricated tips are then removed from the holder and mounted on different types of AFM microscopes to perform scanning probe microscopy and infrared scattering SNOM, reported elsewhere. Here we instead focus on the PL emission, of these tips at the Ge energy gap, detected using a scanning confocal optical microscope setup.

Figure 2. Confocal photoluminescence setup. The emitter (in this case the epitaxial Ge tip, top right inset) is scanned in space along x , y and z . For each point, either the integrated PL emission or a specific wavelength-dispersed component is measured. On the left, representative maps for different values of the z coordinate. The polarization direction of the excitation beam can also be varied (E_1 , E_2).

Photoluminescence emission

We used a home-made far-field confocal microscopy setup to record spatial maps of the spontaneous PL emission from Ge at its direct energy gap,, employing a standard long-working-distance achromatic objective (N.A. = 0.7) and an excitation diode laser emitting at $\lambda_0 = 785$ nm. A typical diffraction-limited image of one of the tips mounted in the confocal microscope, obtained by detecting the scattered light at $\lambda_0 = 785$ nm, is shown in Fig. 1c. The average power impinging on the objective during PL measurements is kept in the 1-10 mW range, corresponding to a power density of about 10^4 - 10^5 W/cm². The different spectral components of the collected PL emission (free of scattering background) are separated inside a Pellin-Broca (P-B) prism and then focused onto an InGaAs/InP single-photon avalanche diode (SPAD), whose active area (25 μ m diameter) acts both as a spectral and a spatial filter in the image plane for wavelength selection and background rejection, respectively. The spectral resolution is about 15 nm in the spectral range of interest around 1550 nm.

Figure 3. Photoluminescence emission collected in a 20 nm band around 1550 nm from an epitaxial Ge tip, while exciting wavelength of 785 nm. (a,b) PL maps for the excitation field E polarized parallel/perpendicular (E_1/E_2) to the pyramid axis. (c) Linescan corresponding to the dashed line in panel (a).

Representative photoluminescence maps obtained by selecting a spectral window around 1550 nm are shown in the left part of Fig. 2 for different positions of the tip with respect to the focal plane along the optical beam propagation coordinate z : the strongest PL emission appears at $z = 0$, and it immediately drops for $z = \pm 0.5$ μ m indicating an emitter size that is comparable with the wavelength of light. The tip appears almost as a Gaussian source because of the convolution between the nanostructure and the tightly-focused illumination beam. However, a careful observation of Fig. 3a reveals a deviation of the spot shape from that of a circle (that can be conversely observed when illuminating the unprocessed pillars, see below) to that of a triangle with its upper apex pointing upwards in the image. This shaping effect, which is the result of the above-mentioned convolution demonstrates that the lateral resolution of the microscope is indeed comparable with the pyramid size. A confirmation to this claim comes from the linescan in Fig. 3c that shows a full width at half-maximum of the intensity detected during the confocal scan of 970 nm $\approx 0.7 \lambda$. Moreover, as we will see below, electromagnetic simulations predict that enhanced PL emission is expected at the tip apex.

Figure 4. Simulations of the excitation intensity beam inside and around the pyramidal tip. Side illumination from the positive z direction is assumed, as in the actual experiment. Electric field polarization direction is E_1 i.e. along the y axis (pyramid axis).

The effect of field enhancement provided by the sharp apex can be appreciated by looking at the two xy maps in Fig. 3a and 3b, taken in identical conditions apart from the electric field polarization direction of the excitation beam at 785 nm. In Fig. 3a, the PL emission at 1550 nm is reported for the electric field polarization direction E_1 which was determined to be almost parallel to the tip axis. In Fig. 3b, the orthogonal direction E_2 was employed. One observes a clear dependence of the emitted intensity on the linear polarization direction of the excitation beam, that could in principle be related to different optical modes of the tip at the emission wavelength. However, the PL emission phenomenon does not keep memory of the excitation beam polarization, since the electron excited by the absorbed photon of wavelength λ_0 decays through a large number of non-radiative transitions to an energy minimum of the conduction band, before recombining with a hole, producing PL emission at $\lambda < \lambda_0$. In other words, the probability for an excited electron-hole pair to decay into a mode of the tip-shaped ‘cavity’ with specific polarization properties is independent of the polarization of the excitation beam. The PL emission efficiency is then expected to be identical for the two polarization directions. Therefore, the higher emission seen for direction E_1 has to be related to a more efficient absorption of the excitation beam inside the epitaxial tip, pointing towards lightning-rod field enhancement effects at the tip apex when the electric field is directed along the pyramid axis. Such effects are very well understood for metallic tips whose optical response is dominated by conduction currents [REF: L. Novotny and S. J. Stranick, “Near-field optical microscopy and spectroscopy with pointed probes”, *Annu. Rev. Phys. Chem.* **57**, 11.1-11.29 (2006)] but can be as well observed in dielectric tips that are characterized by localized polarization currents.

A quantitative analysis of the measured PL emission is performed with the aid of electromagnetic simulations based on the finite-difference time-domain method (FDTD Solutions, Lumerical Inc., Canada) to derive whether the emission properties of the epitaxial material were preserved or degraded by the fabrication process. The tip is modeled as a Ge pyramid on a Si shaft and standard tabulated dielectric function values were used for both Si and Ge. First, we simulated the electric field enhancement at $\lambda_0 = 785$ nm (see Fig. 4) and the corresponding absorbed power density. Then we simulate the emission process by placing a

number of randomly oriented emitting dipoles proportional to the absorbed power density inside the tip, with a method already validated in previous publications [20]. It is important to stress that, in order to mimic the incoherent emission process and avoid spurious interference effects between dipoles, N individual simulations need to be run to calculate the emission from N different dipoles. Finally, we integrate the emitted intensity within the collection solid angle of the objective and compare it to the integrated experimental PL emission intensity to get an estimate of the PL efficiency.

The simulated emission intensity calculated for the N dipoles mimicking the PL process misses some pre-factors (e.g. related to the overall throughput of the experimental setup or to the intrinsic efficiency of the PL emission process) that we can eliminate by benchmarking the tip emission against the emission of a well-defined structure made of the same material and measured in the same setup. To this aim, we investigated some of the pillars which were etched on the same Ge/Si wafer used for tip fabrication. In our tip fabrication process, only one of many nominally identical pillars formed by etching the epitaxial layers is lifted out of the wafer with the AFM cantilever. The pillars that were not lifted-out indeed represent a sample of exactly the same epitaxial material as that of the tip, which did not undergo the FIB-based fabrication process. The PL map of a portion of the pillar field, taken in the same experimental setup as Fig. 2 and 3, is shown in Fig. 5. It shows circular spots, compatible with the circular cross-section of the pillars, clearly due to PL emission from the top Ge epitaxial layers (it can be seen in Fig. 5 that the much larger Si structures produce negligible PL emission at 1550 nm). Electromagnetic simulations were run also for the pillars (Fig. 6) and the PL emission efficiency was calculated using the same procedure described for the tip simulations. Considering the dimensions of the focal spot and the different absorption and emission properties for the pillars and the tip, the power fraction emitted inside the collection angle of the objective from the pillar is calculated from FDTD simulations to be about 4 to 5 times higher than that from the tip, an effect that is mainly due to the larger volume of the pillars compared to that of the tip. Experimentally, we found that the integrated PL emission collected from the pillar actually exceeds that collected from the tip by a factor of about 4.5, demonstrating an excellent agreement with the simulations and confirming that no significant effects such as e.g. luminescence quenching due to FIB-induced surface defects takes place.

Figure 5. Photoluminescence emission from two pillars etched on the epitaxial Ge/Si wafer used for tip fabrication. The bottom of the image displays the PL background from three Si structures contaminated by Ge residues of the pillar etching. The inset is a zoom from one of the pillars.

Figure 6. Simulations of the excitation beam intensity inside and around a Ge pillar on the Si wafer. Top-illumination from the z direction is assumed.

The nanoscale photon sources based on semiconductor PL presented here could be employed in a number of possible applications. A first one is the optical coupling single quantum emitters to field-enhancement devices such as photonic crystal cavities and plasmonic concentrators. Indeed, it is now established that fluorescent quantum emitters strongly couple to guided modes and to surface plasmons when located in the proximity of a cavity or of a metallic structure. In this context, position-control of the emitter location by AFM technology is a premium feature of our device. The scanning PL source would enable to map the local density of electromagnetic states (LDOS) for example to characterize plasmonic nonradiative dark modes or cavity modes that do not strongly couple to propagating modes. Indeed, an accurate map of the LDOS should include all types of electromagnetic states: states coupled to the free space by radiative decay into the far field, but also near-field coupled states that decay into confined resonances, and non-radiative states in general. After having imaged the LDOS of a resonator or cavity, one can also take advantage of the scanning PL source to position it at the optimal location for the fabricated structure, as retrieved from the LDOS map.

Finally, the fundamental understanding of the PL emission process together with the precise position control provided by AFM piezo-stages could lead to significant advances in on-chip quantum communications by connecting the macroscopic world of single-photon propagation to nanoscale devices eventually capable of quantum computation. In this respect, the fact that our scanning Ge-PL source emits exactly at the long-haul fiber-optics network wavelength of 1550 nm is certainly a premium feature.

Conclusions

This work demonstrates PL emission from a scanning probe tip made of epitaxial semiconductor material. The epitaxial Ge tips was mounted in a confocal micro-PL emission setup, where an illumination wavelength of 785 nm excites electron-hole pairs in the Ge tip that subsequently radiatively recombine at the direct energy gap of Ge (0.86 eV, 1550 nm). The PL emission was dispersed in a home-made spectrometer working in the near-infrared range (800-1700 nm) and detected via an InGaAs/InP avalanche diode as the tip was raster scanned in the focal point of the microscope objective. A strong and tightly-confined emission was recorded from the tip apex. Comparison between the PL emission of the pillar (before fabrication) and of the tip (after fabrication) demonstrated that the PL yield is not significantly affected by fabrication, indicating that the optical properties of the material in this wavelength range were preserved during the FIB milling process.

Acknowledgements

This work was partially funded by the Italian Ministry of Research through the program SIR (Grant No. RBSI14IT0D) and by Fondazione Cariplo through the project SHAPES (id: 2013-0736). The research leading to these results has received also funding from the European Union's Seventh Framework Programme under grant agreement n°613055. Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231, proposal n°1773.

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