Physica C: Superconductivity and its applications 552 (2018) 34–37

Contents lists available at ScienceDirect

Physica C: Superconductivity and its applications

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

Quantum constriction at the interface between a superconducting nanocrystal and an electron accumulation layer

Sergio Vlaic[a], Stéphane Pons[a], Tianzhen Zhang[a], Alexandre Assouline[a], Alexandre Zimmers[a], Dimitri Roditchev[a], Hervé Aubin[*,a], Christophe David[b], Guillemin Rodary[b], Jean-Christophe Girard[b]

[a] CNRS, Sorbonne Universités, UPMC University of Paris 6, LPEM, ESPCI Paris, PSL Research University, 10 rue Vauquelin, Paris F-75005, France
[b] Centre de Nanosciences et de Nanotechnologies, CNRS, University of Paris-Sud, Universités Paris-Saclay, C2N Marcoussis, Marcoussis 91460, France

ARTICLE INFO

Keywords:
elsarticle.cls
LaTeX
Elsevier
Template

MSC:
00-01
99-00

ABSTRACT

In the recent work of Vlaic et al. (2017), it has been shown that Pb nanocrystals (NCs) grown on the electron accumulation layer at the (110) surface of InAs are in the regime of Coulomb blockade. This enabled the first Scanning Tunneling Spectroscopy (STM) study of the superconducting parity effect across the Anderson limit. The observation of Coulomb blockade implies the existence of a tunnel barrier between the NCs and the substrate. This tunnel barrier has been ascribed to a quantum constriction of the electronic wave function at the interface between the NCs and the electron accumulation layer owing to its large Fermi wavelength. In this proceeding, we detail and review the arguments leading to this conclusion.

1. Introduction

In a nanocrystal (NC) of volume V, the mean level spacing is given by:

$$< \delta > = \frac{2(\pi\hbar)^2}{m^* k_F V}. \quad (1)$$

This relation shows that for low carrier density materials with small Fermi wavenumber k_F, such as weakly doped semiconducting quantum dots (QDots), the level spacing is large. For this reason, the regime of quantum confinement has been intensively studied in semiconducting QDots, either in colloidal QDots [2–5] or in microfabricated QDots [6–11]. In contrast, the study of quantum confinement in high carrier density materials, such as metals or superconductors, is much more challenging. For lead (Pb) with a Fermi energy E_F = 9.4 eV, two Fermi surfaces FS_1 and FS_2, of characteristics wave-vectors $k_{F1} = 7.01$ nm^{-1}, $k_{F2} = 11.21$ nm^{-1} and effective mass $m^* = 1.2$ m_e, at the temperature T = 1.3 K, i.e. thermal broadening $k_B T = 112\,\mu$ eV, a discrete electronic spectrum on the two Fermi surfaces is expected for NCs volume smaller than 1000 nm^3, i.e. a sphere of diameter 25 nm.

STM is particularly well adapted for a tunnel spectroscopy of NCs. The instrument can provide both a topographic image of the NC being studied and spectroscopic data with atomic resolution. While numerous works exist on the STM study of UHV grown metallic clusters strongly coupled to the substrate [12], the study of quantum confinement effects in isolated ultra-high vacuum (UHV) grown NCs has been hampered by two contradicting requirements: on the one hand, the substrate should be conducting enough to enable a current path to the ground; on the other hand, the NCs should also be separated from this substrate by a second tunneling barrier, to preserve quantum confinement.

To enable the growth of high quality crystalline NCs, this second tunnel barrier should present a well ordered surface. While tunnel barriers on a metallic substrate can be formed by oxidation, the deposition of a dielectric [13] or the formation of a self-assembled molecular layer, these *extrinsic* tunnel barriers usually present poor atomic orders not suitable for the growth of crystalline NCs. To avoid the use of these extrinsic tunnel barriers, growing metallic NCs on semiconductors to employ the *intrinsic* tunnel barriers that may exist at the metal-semiconductor interface seems more promising. While the usual Schottky barriers found at metal-semiconductor interfaces are too opaque to enable electron tunneling at low energy, < 1 eV, we found that a tunnel barrier also exists at the interface between an electron accumulation layer and the NCs when their size is smaller than the Fermi wavelength of the accumulation layer. In contrast to the Schottky barrier, this tunnel barrier is transparent enough to enable tunneling at low energy.

* Corresponding author.
E-mail address: herve.aubin@espci.fr (H. Aubin).

https://doi.org/10.1016/j.physc.2018.05.013
Accepted 7 March 2018
Available online 05 July 2018
0921-4534/

2. Nanocrystal growth

The growth of NCs is done on the (110) surface of InAs, for which an STM image with atomic resolution is shown Fig. 1(a). This surface is obtained by cleaving an ⟨001⟩ oriented substrate, which is n-doped with sulfur to a carrier concentration of $N_D \simeq 6 \times 10^16$ cm^{-3}. The Pb NCs are obtained by thermal evaporation of a nominal 0.3 monolayer of Pb on the substrate heated at $T = 150$ °C.

As shown on the topographic images, Fig. 1, Pb grows in the Volmer–Weber, i.e. island mode [12]. For this proceeding, we will focus on the six NCs shown Fig. 1(c)–(h). The corresponding differential images $\nabla_{xy}z$, Fig. 1(i)–(l), for the 4 largest NCs, show that the NCs are well crystallized and expose mostly the (111) planes of the cubic face-centered Pb structure, as indicated by the observation of the characteristic hexagonal shape of the (111) facets. Surrounding these NCs, the surface remains free from any adsorbate and atomic resolution on the (110) InAs surface is possible.

The shape of the NCs is mostly pyramidal as sketched Fig. 1(m), where the [001] direction of Pb is oriented perpendicular to the substrate. For this geometry, the height of the NC is given by $h = n \times u_{\text{cell}}/2$ where $u_{\text{cell}} = 0.495$ nm is the length of the unit cell of Pb; $u_{\text{cell}}/2$ is the distance between atomic rows along the [001] direction of Pb, which has a Face Centered Cubic (FCC) structure, and n is the number of atomic rows.

3. Metal-semiconductor interfaces

Following [14], we describe the expected nature of the interface Pb/InAs (110).

Generally, the adsorption of a metal overlayer leads to band-bending in the semiconductor. The barrier height ϕ_{Bn} for the electrons in the conduction band is given by the relation:

$$\phi_{\text{Bn}} = S_\phi(\phi_{\text{m}} - \chi_{\text{s}}) + (1 - S_\phi)\phi_{\text{B0}} \tag{2}$$

where ϕ_{m} is the metal work function, χ_s is the semiconductor electron affinity, $S_\phi = \frac{\partial\phi_{\text{Bn}}}{\partial\phi_{\text{m}}}$ is the slope parameter. This last parameter describes the dependence of the barrier height on the metal work-function. When no interface-induced gap states are present, the barrier height is given by the well-known Schottky–Mott formula, where $S_\phi = 1$. In this case, the barrier height is strongly dependent on the metal work function. In the other extreme limit, called the Bardeen limit, $S_\phi = 0$, the Fermi level is pinned by interface states. In that case, the barrier height does not depend on the metal work function, it is given by $\phi_{\text{B0}} = W_{\text{ci}} - W_{0\text{i}}$ where W_{ci} is the energy of the bottom of the conduction band and $W_{0\text{i}}$ is the charge-neutrality level of the continuum of interface states; the Fermi level coincides with this charge-neutrality level. The charge-neutrality level separates the electron-type levels from the hole-type levels. As described in Refs. [14–17], because the metal-induced interface states into the semiconductor derive from the band structure of the semiconductor, the charge neutrality level is only a property of the semiconductor, which implies that the barrier height is independent of the metal work function.

The interface of III–V semiconductors with adsorbates of different kinds has been investigated extensively. For most III–V semiconductors such as GaAs, the charge neutrality level lies within the band gap. In that case, the interface between metals and GaAs present a large Schottky barrier that prevents tunneling at low energies (< 1 eV) [18–21].

In contrast, for small gap materials like InAs and InSb, the charge neutrality level lies within the conduction band [15,22–24], which leads to the formation of an accumulation layer of electrons at the surface. For InAs (110), the Fermi energy is about 100–400 meV above the conduction band minimum. This has been found for very different adsorbates such as H, O, N, Cl, Ag, Au, Ga, Cu, Cs, Na, Sb, Nb, Fe and Co.

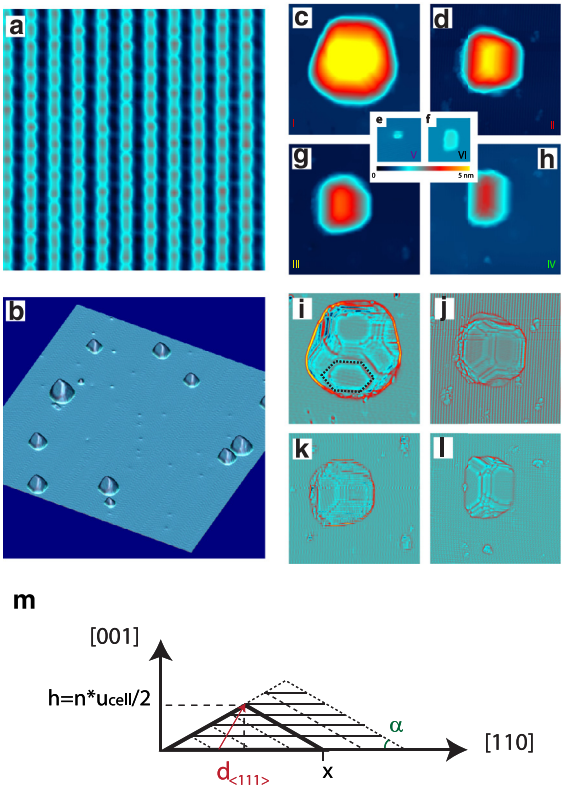

Fig. 1. (a) 6.5 nm × 6.5 nm atomic resolution image of InAs (110). (b) 3D 150 nm × 150 nm topographic STM image (1 V, 30 pA) of Pb NCs grown on the (110) InAs surface. (c)–(h) 6 topographic images of NCs of different sizes shown on the same *x*, *y* and *z* scales. (c), (d), (g) and (h) are 30 nm × 30 nm, while (e) and (f) are 10 nm × 10 nm. (i)–(l) are Laplacian $\Delta_{xy}z(x, y)$ images of NCs, corresponding to the topographic images (c), (d), (g) and (h). The hexagonal dash line on panel (i) is guide to eye to highlight the hexagonal shape of the facets of the NC. (m) Sketch of the pyramidal NC indicating the main crystallographic directions.

4. Coulomb blockade and parity effect

Fig. 2 shows the differential conductance (DC) measured on the six NCs shown Fig. 1. In the same figure, the volume of the NCs is indicated in units of $V_{\text{Anderson}} = 100$ nm^3. The DCs for the five larger NCs display a Coulomb gap at zero bias of width $\delta V_{\text{sub}} = e/(C_{\text{sub}} + C_{\text{tip}})$ where C_{sub} (C_{tip}) is the capacitance between the NC and the substrate (tip). These DCs also display sharp Coulomb peaks where the voltage interval between the peaks provides the addition voltage δV_{add} for an electron, which is related to the addition energy by : $\delta V_{\text{add}} = E_{\text{add}}/e\eta$ where $\eta = \frac{C_{\text{tip}}}{C_{\text{tip}} + C_{\text{sub}}}$ is the arm lever; see Ref. [1] for a derivation of these relations. Fig. 2(b), obtained from Ref. [1], shows that C_{sub} extracted from the Coulomb gap at zero bias is a linear function of NC area A.

The addition energy, i.e. the energy for adding one electron into the NC, is given by:

$$E_{\text{even(odd)}} = \frac{e^2}{C_\Sigma} + (-)2\Delta + \delta \tag{3}$$

where the first term is the Coulomb energy, the second term depends on the parity of electron occupation number as a consequence of the formation of a Cooper pair [25,26], the third term is the electronic level spacing in the NC.

Thanks to the quality of the tunnel barrier enabling very sharp Coulomb charging peaks, it has been possible to study, for the first time by STM, the evolution of the superconducting parity effect in the addition energy across the Anderson limit [1]. Fig. 3 shows representative spectra as function of temperature, measured on NC IV shown Fig. 1.