Growth and low temperature photoluminescence of silicon nanowires for different catalysts.

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Growth and low temperature photoluminescence of silicon nanowires for different catalysts.

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ABSTRACT

We report the growth of silicon nanowires (SiNWs) by chemical vapor deposition (CVD) with several catalysts. We performed low temperature photoluminescence (PL) experiments on as-grown SiNWs for the following catalysts: Au, Cu, TiSi, PdSi and PtSi. Nanowires are chemically treated with an aqua regia solution to remove the catalyst droplets, this step is followed by a thermal oxidation process. We compared the PL of as-grown and processed SiNWs for each catalyst.

INTRODUCTION

Silicon nanowires (SiNWs) have attracted a large scientific interest as promising new structures for various applications such as nano-sensors or for electronics and opto-electronics devices thanks to their very interesting integration properties. As an alternative to top-down approach by etching techniques, SiNWs can be produced by Chemical Vapor Deposition (CVD) via the Vapor-Liquid-Solid (VLS) or the Vapor-Solid-Solid (VSS) mechanisms [1-4]. The catalytic materials at the basis of those two growth mechanisms can be of various sort and their influence on SiNWs properties remains to be probed.
In this paper we propose a systematic study of growth and photo-luminescence (PL) properties of CVD SiNWs using the following catalysts: Au, Cu, Ti, Pt and Pd. The PL of as-grown SiNWs is compared to that from thermally oxidized nanowires.

EXPERIMENT & RESULTS:

Nanowire growth and oxidation:

Silicon nanowires were grown in a Low Pressure Chemical Vapour Deposition (LPCVD) reactor using a H2 carrier gas flow at 20mbar. All samples are grown on Si [100] substrates. Si wafers were first deoxidized in a HF 10% solution for 1 min before catalyst deposition. Depending on the material, catalysts were evaporated as thin film by Joule heating: Au and Cu, or sputtering: Pt, Pd, Ti. For PdSi and PtSi a supplementary annealing step was performed to form PdSi and PtSi silicide before the CVD deposit.

The typical deposit sequence consists in a 1) a H2 annealing step at 800°C-900°C substrate temperature at 20mbar 2) a deposit step using SiH4 and HCl, at 650°C-800°C substrate temperature, in H2 carrier flow at 20 mbar. Table 1 summarizes growth conditions for

each catalyst studied. The geometrical aspects are also reported: tapered NWs are distinguished from the non-tapered, dimensions concern the diameter dispersion for non-tapered NWs and the order of magnitude of the tapering of other NWs.

Catalyst	H2 Annealing	Deposit step	p(SiH4)	p(HCl)	Geometrical aspects
Au	850 °C (10 min)	650 °C (50 min)	0.25 mbar	0.5 mbar	Non-tapered 100-200 nm
Cu	900 °C (5 min)	750 °C (15 min)	0.125 mbar	0.125 mbar	Tapered 100-2000 nm
Cu	900 °C (5 min)	750 °C (30 min)	0.125 mbar	0.25 mbar	Non-tapered 100-300 nm
Ti	900 °C (5 min)	750 °C (15 min)	0.125 mbar	0.125 mbar	Tapered 100-300 nm
PdSi	800 °C (15 min)	800 °C (15 min)	0.125 mbar	0.125 mbar	Non-tapered 50-200 nm
PtSi	800 °C (15 min)	800 °C (25 min)	0.125 mbar	0.125 mbar	Tapered 100-1000 nm

Table 1: Experimental condition used for the CVD growth of SiNWs. p(SiH4) and p(HCl) are respectively SiH4 and HCl partial pressures. Total reactor pressure is 20mbar in a H2 atmosphere.

During the VLS or the VSS process, Si material is brought to the wire via a gas phase Si precursor which decomposes on the metal catalyst. This steady source of Si first alloys the catalyst into a Metal-Si alloy (M-Si), Metal being either Au Cu Ti Pt or Pd, and then supersaturates the M-Si catalyst with Si material. Excess of Si is evacuated from the catalyst by the precipitation of a pure Si phase, which forms a Si column below the catalyst. At the end of the deposit step, the system consists in a long Si column, ie. the Si wire, terminated by a small M-Si catalyst.

Depending on the CVD growth temperature used in the deposit step and the M-Si phase diagram, the catalyst can be either in the liquid or solid state. Data is summarized on table 2 for each type of used catalyst. As most metals present at least one eutectic with Si, table 2 only reports the temperature of the most Si saturated eutectic point in the phase diagram.

Catalyst	Eutectic Temperature	Growth Temperature	Catalyst phase
Au	363 °C	650 °C	liquid
Cu	802 °C	750 °C	solid
Ti	1330 °C	750 °C	solid
PdSi	980 °C	800 °C	solid
PtSi	870 °C	800 °C	solid

Table 2: Eutectic temperature of M-Si alloys in the Si rich part of the phase diagram [??]. Depending on the growth temperature used in the CVD deposit catalyst can be either liquid or solid. Most M-Si catalyst used are in the solid state during wire growth, Au-Si being the only liquid.

The main differences between Vapour Liquid Solid and Vapour Solid Solid mechanism, respectively solid and liquid catalyst, are 1) the Si diffusion constant in the M-Si phase, which is quicker in the liquid than in the solid and 2) the epitaxial relation between the Si column and a solid M-Si phase, which is replaced by a surface energy term in presence of a liquid M-Si phase. Figure 1 shows SEM images of the obtained SiNWs. Depending on the catalyst used for the growth, the wires are either straight or tapered. Tapering can be independent of VLS/VSS type of growth as PdSi wires, fig 1.e, present straight sidewalls while PtSi wires, fig 1.f, present tapered

sidewalls in similar conditions (see table 1). Keeping the same catalyst, tapering can also be adjusted by the HCl partial pressure. As shown on fig 2.b and 2.c on Cu catalysts, mid HCl partial pressure favours straight sidewall while low HCl partial pressure results in tapered wires. This observation is also valid for Au-catalyzed wires, fig 1.a, which can be grown over very large length, 80 µm, without Au droplet loss or tapering using a high HCl partial pressure (0.5 mbar).

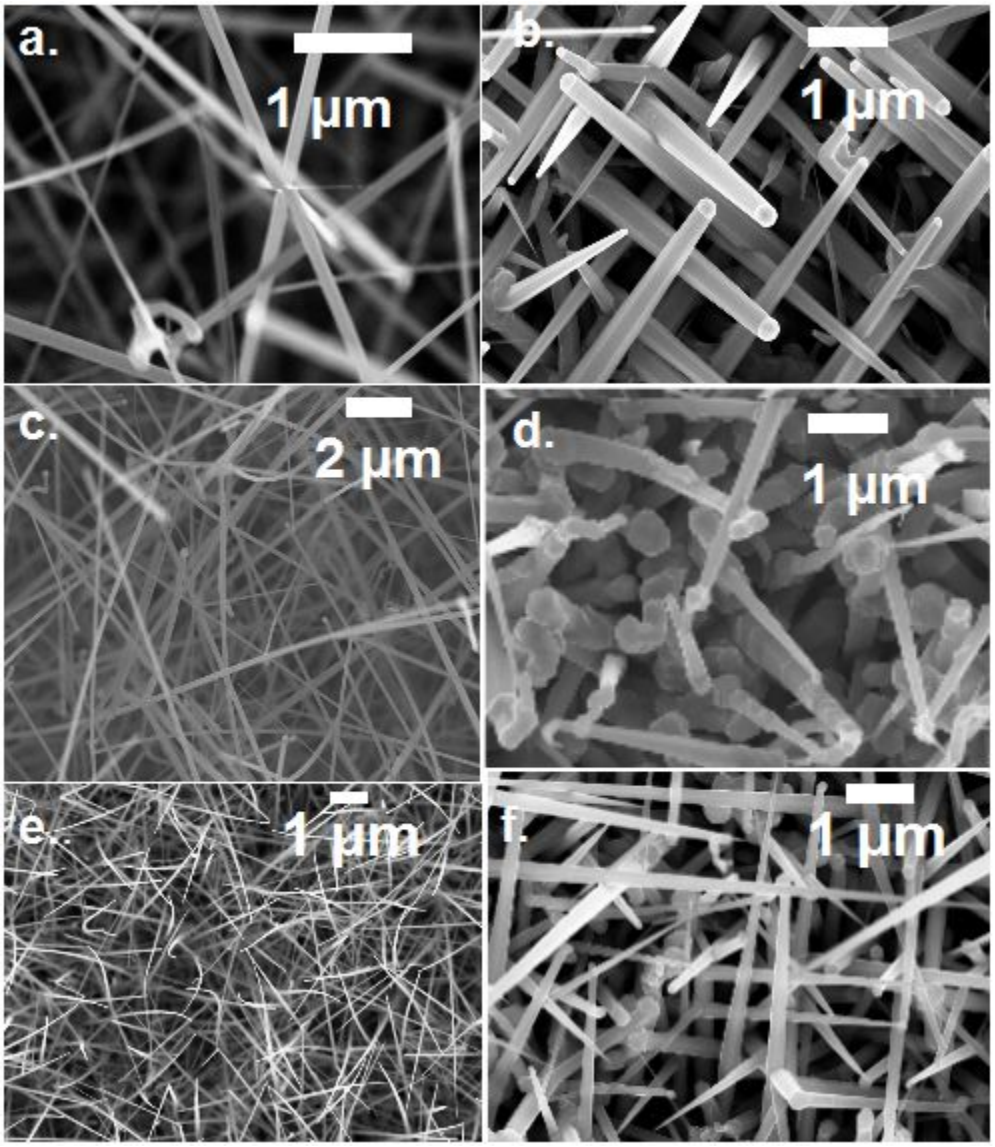

Fig.1 SEM images of the obtained SiNWs. 1.a Long Au-catalysed SiNWs grown at very high HCl partial pressure (0.5 mbar). 1.b Cu-catalyzed wires grown at low HCl partial pressure (0.125 mbar). 1.c Cu-catalyzed wire grown at mid HCl partial pressure (0.25 mbar). 1.d Ti-catalysed wires grown at low HCl partial pressure (0.125 mbar). 1.e PdSi-catalyzed wires, grown at low HCl partial pressure (0.125 mbar) . 1.f PtSi-catalyzed wires grown at low HCl partial pressure (0.125 mbar).

A first set of photoluminescence experiments (PL) were performed directly after growth to acquire as-grown spectra of the wires, figure 2. After these first PL experiments, the samples were chemically treated to remove metal catalyst and native oxide by dipping in the following baths 1) 49% HF, 1 minute, 2) aqua regia bath (HCl(37%) : HNO3(70%), 2:1), 15min, 3) 49% HF, 1 minute. Samples were subsequently oxidized in a furnace at 900°C under 10 mbar O_2 flow during 20 minutes. The samples were allowed to cool down to room temperature in the furnace under 10 mbar forming gas (H_2:N_2, 5:95) flow during 3 hours. The resulting thermal oxide thickness is measured to be 5 nm on a <100> silicon substrate. Due to the large diameters of the SiNWs and the small oxide thickness, we assume the thicness of SiO2 shell to be close of 5 nm. A second set of PL experiments was then carried out to obtain the spectra of the oxidized nanowires, figure 3.

Photoluminescence:

The samples are optically pumped with the 355 nm line of a pulsed triple Nd:YAG laser. Pulses are 10 ns long, and the repetition rate is of 6 kHz. Laser beam is focused on a spot of 500 µm. Samples are cooled down in a liquid helium circulation cryostat allowing a temperature control from 4.2 K up to 300 K. The SiNWs luminescence is analyzed in the Infra-Red range (0.9-1.3 eV) with an InGaAs CCD where silicon indirect bandgap luminescence is expected. Indeed, the silicon bandgap energy at low temperature is of 1.17 eV, and the more intense radiative recombination of free excitons is the transverse and longitudinal optical phonon-assisted recombination at 1.096 eV.

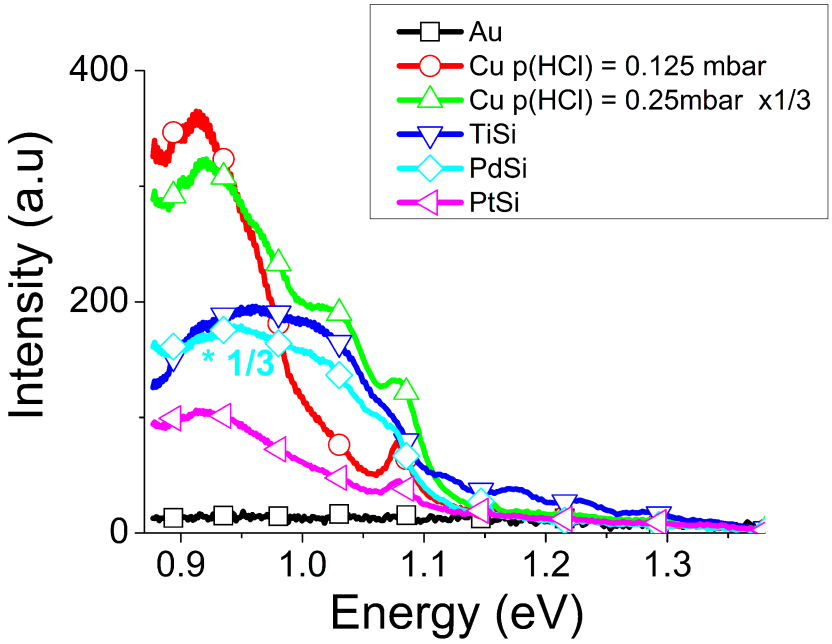

Fig.2 Photoluminescence of as-grown SiNWs whose catalysts are indicated in the legend. The temperature of experiments is of 5 K and the optical pump power is of 0.8 µJ per pulse.

Fig.2 shows the photoluminescence spectra obtained at 5 K from as-grown SiNWs for an optical pump power of 0.8 µJ per pulse. The PL spectrum of Au-catalyzed SiNWs shows no signal in the observed energy range. For PtSi- and the two Cu-catalyzed SiNWs, a peak appears around 1.08 eV which can be attributed to the presence of a condensed phase of carriers: an electron-hole plasma, as it has already been observed in silicon and is explained by coulombian interactions which induce a gap renormalization [5-8]. Except gold, whatever the used-catalyst, SiNWs exhibit a luminescence band between 0.87 eV (the cut-off energy of the CCD) and 1.05 eV which is attributed to near-gap traps whose origin could be due to structural defects in the silicon crystal, surface states or catalyst particles incorporated in nanowires, but is not understood at this time.

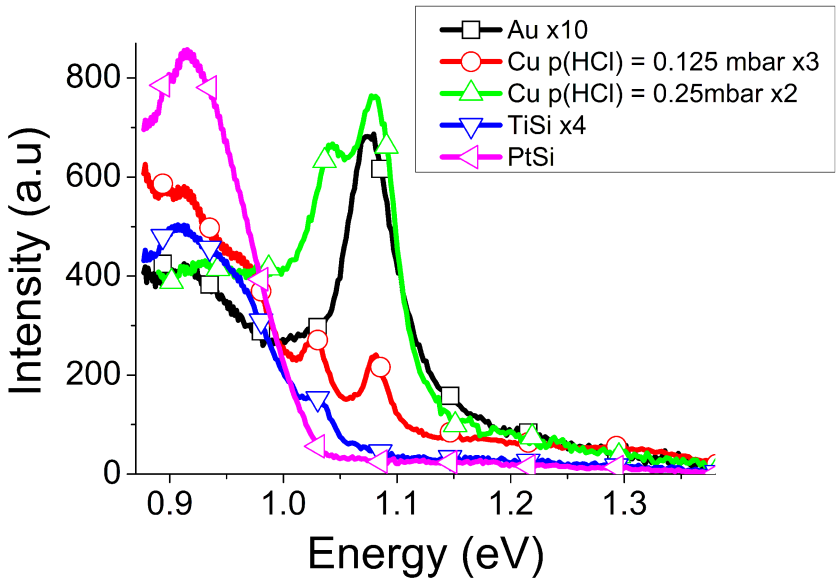

Fig.3 Photoluminescence of oxidized SiNWs grown with the catalysts indicated in the inset. The temperature of experiments is of 5 K and the optical pump power is of 0.8 µJ per pulse.

Fig.3 shows the photoluminescence spectra of oxidized SiNWs. Au-SiNWs are now luminescent and the oxidation allows PL contribution at 1.08 eV which is also clearly enhanced in the PL spectra of both Cu-catalyzed SiNWs. On the contrary, it totally disappears for TiSi- and PtSi-SiNWs. In Cu- and Au-catalyzed SiNWs, chemical treatments associated to the oxidation step allow the observation of a PL line at the same energy than the electron-hole plasma recombination energy. Indeed, this process passivates mid-gap surface states and then some carriers can be free in those SiNWs, not in TiSi- and PtSi-SiNWs. Indeed, the aqua regia solution eliminates with efficiency Cu and Au particles. On the contrary, that solution does not remove accurately TiSi- and PtSi-catalysts from the top of the SiNWs. Oxidation step induces then a diffusion of catalysts particles through nanowires and thus new recombination channel via deep level traps appears. Furthermore, the tappering of those NWs could be due to the progressive incorporation of catalyst particles inside the NWs which could be silicide-NWs.

After oxidation, all nanowires present a radiative emission between 0.87 and 1.05 eV which is still not understood. The presence of catalysts particles incorporated in NWs, of radiative surface states, or radiative structural defects (dislocations for example) could be at the origin of the PL band.

CONCLUSIONS

To conclude, we shown the CVD growth of SiNWs with different catalysts, and the luminescence from as-grown SiNWs. All catalysts except gold induce a luminescence in the near infrared wavelength range. After a passivation step, only copper and gold allow a radiative recombination of free carriers. It could be due to the poor effect of the aqua regia solution to remove the other catalysts. Thus they can diffuse trough nanowires during the oxidation and act as deep level for the carrier recombination. The formation of silicide-NWs with those catalysts could also explain that. Further experiments are needed to identify trap states depending on the nature of the catalyst.

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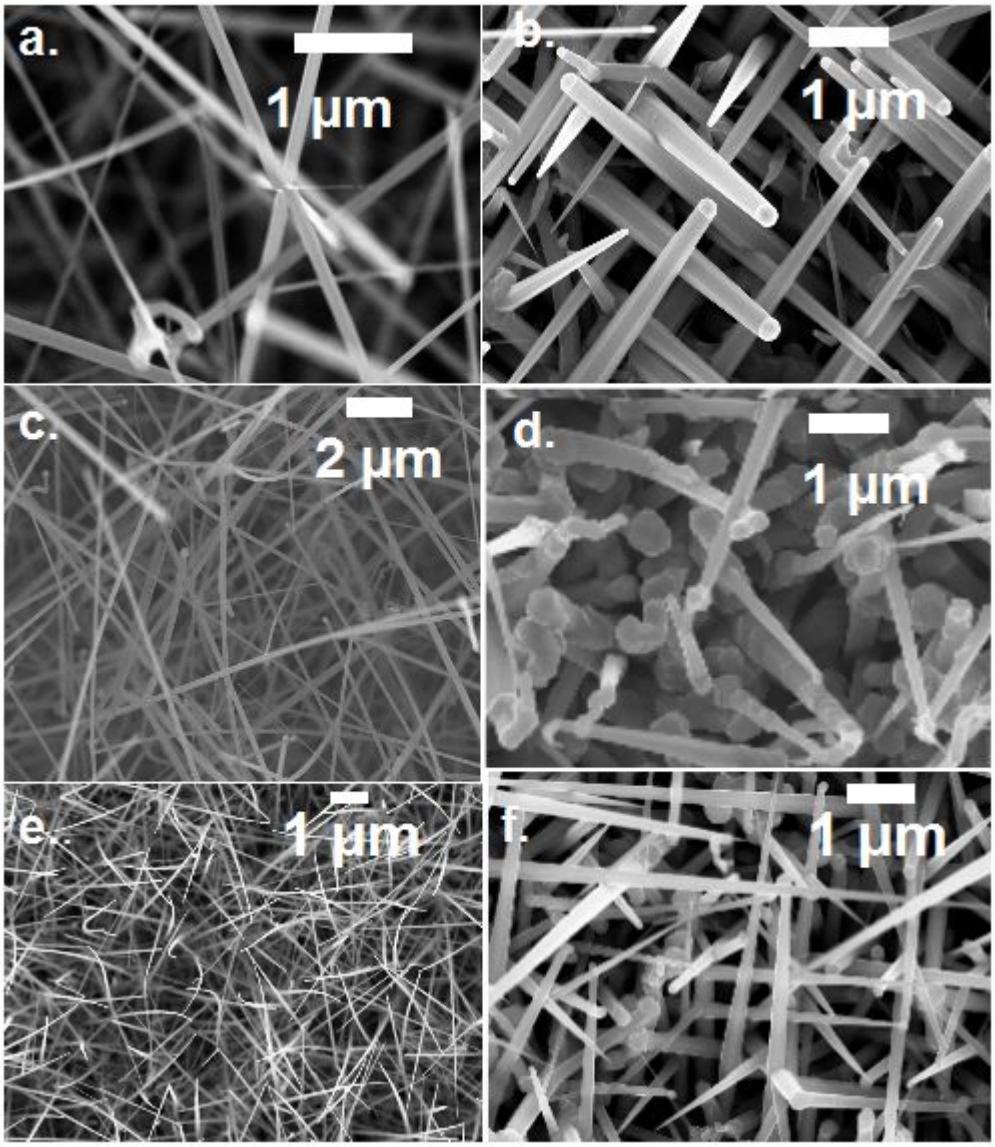

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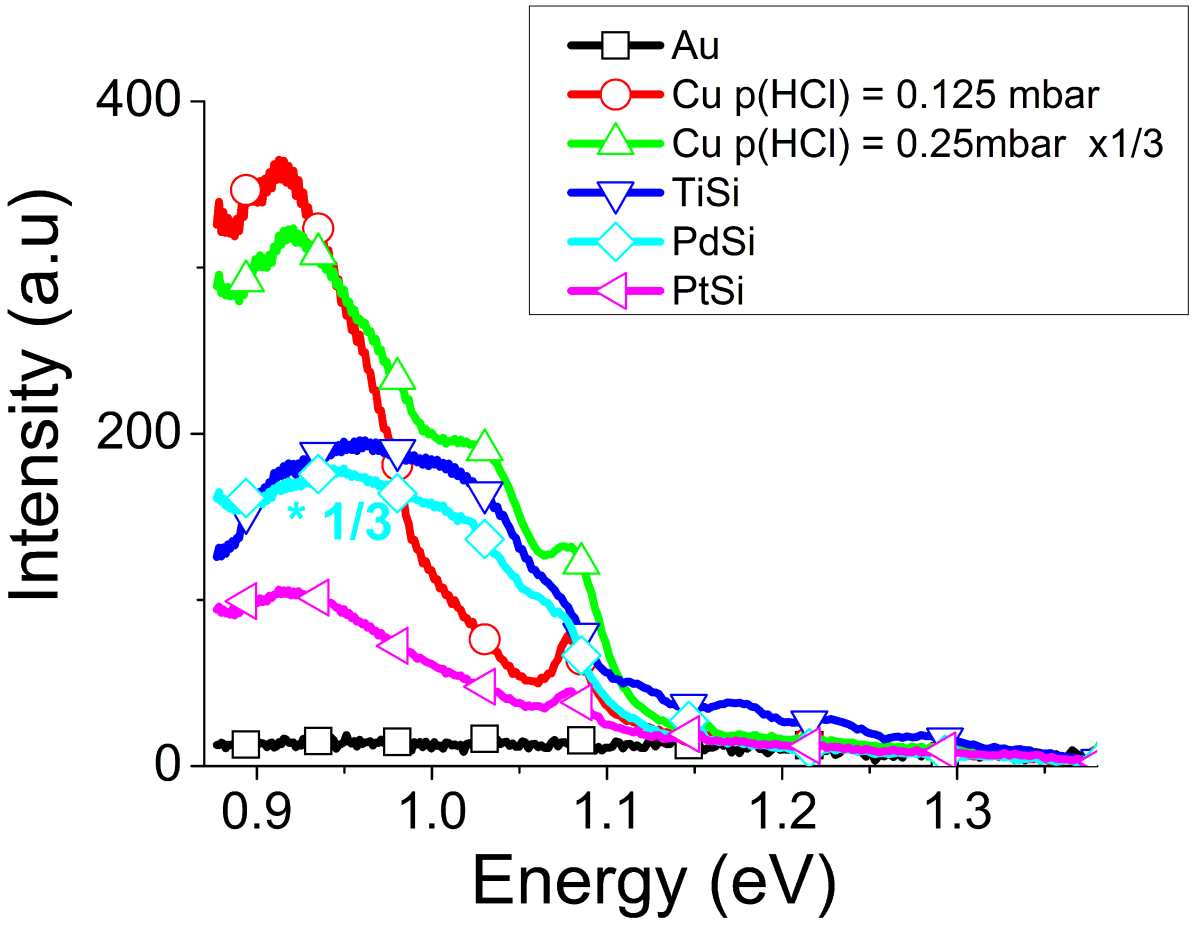

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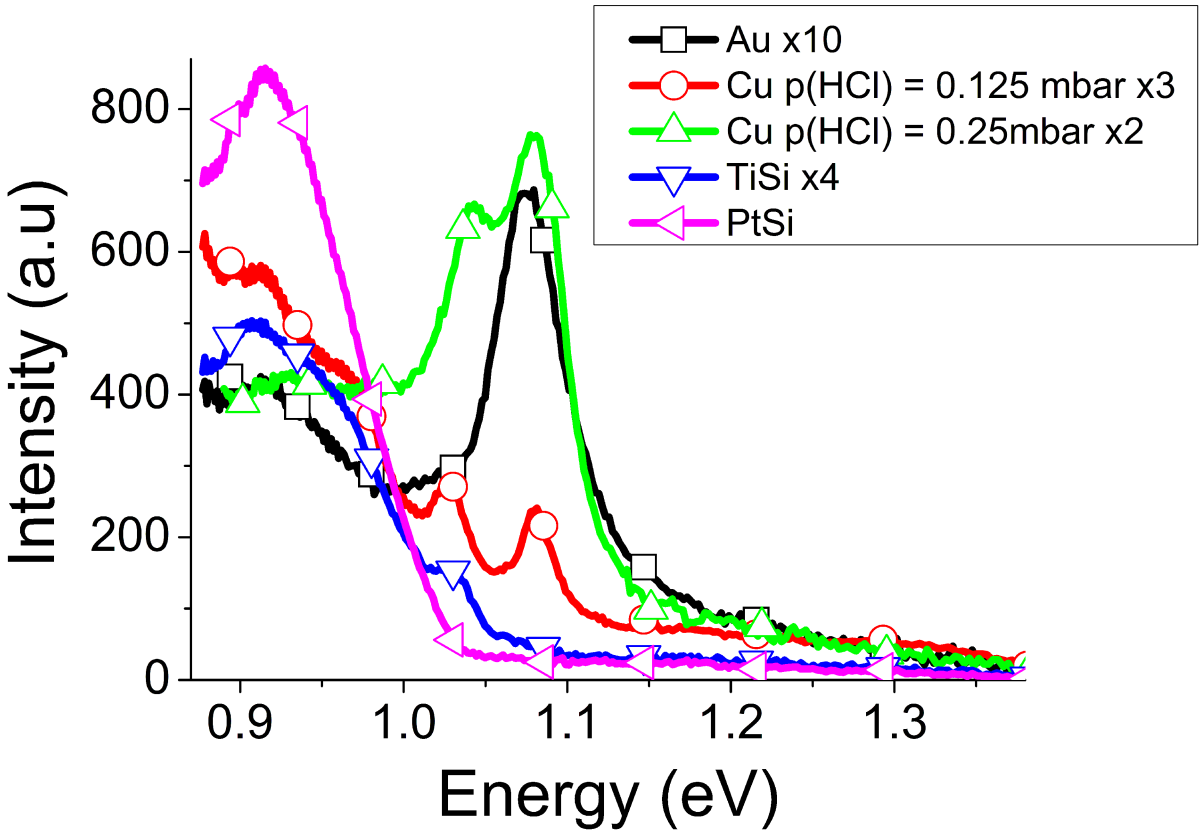

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