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Atomically Defined Metal Nanostructures on a Si(111):H Surface

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In this work, a method developped for the fabrication of "hybrid" lead nanowires on hydrogenated Si(111) specimens by ultra-high vacuum scanning tunneling microscopy is presented for the first time. The nanostructures are characterized by the presence of a new lead phase inside supporting nanolines formed by bombardment of electrons field emitted from a tungsten tip apex in the vacuum gap. Magnified CCT images of the depassivated regions evidence lead ridges distantly spaced of 2 nm, which is about three times that of the chains periodicity on a Si(111) 2x1 π-bonded surface (0.67 nm). A comprehension of ridges structural and electronical features in respect with those of an underlying Si(111) restatom layer is given here in order to promote further theoretical calculations.

Key words: scanning tunneling microscopy, lead, nanowire, silicon, hydrogen.

1.INTRODUCTION

Atomically defined silicon-based nanostructures represent fundamental building blocks for the realization of quantum devices offering optimum operation performances in Tera Hz (THz) regime at room temperature (RT) [1]. Already, atomically defined nanowires have been fabricated on Si(100)2x1 structures with advanced SPM manipulation techniques [2]. Very recently, 2x1 π-bonded chains of silicon atoms reported to usually form on Si(111) and Si(111):H materials after cleavage [3], thermal quenching [4], or *in situ* selective extraction of hydrogen atoms by low energy electron bombardment from a scanning tunneling microscope (STM) tungsten tip under field emission regime [5], have been proposed as promising candidates for the study of lateral electron transports along high symmetry directions via an empty surface state band, revealing the unexpected strategic importance of Si(111) specimens for direct experimental evidence of isotropic and/or anisotropic surface state conductance modes. In addition, Hasegawa et al. confirmed experimentally the occurrence of electrical conduction through the highly dispersive surface state band of a Si(111) $\sqrt{3}x\sqrt{3}$-Ag superstructure formed by *in situ* deposition of a single Ag monolayer (1ML: $7.84x10^{14}$ atoms/cm^2) on Si(111) 7x7 dimer-adatom-stacking-fault (DAS) structural features at high temperature (T>250°C) [6]. In their study, the capability of silicon step edges to act as potential surface scatterers for conduction electrons was briefly underlined. A reasonable and efficient way to avoid such undesirable scattering effects for the measurement of pure surface state conductance signatures may be a direct confinement of superstructures on isolated parts of the specimen surface, more particularly in between localized scattering potentials such as atomic step edges. However, to our knowledge, the fabrication of metal superstructures both confined structurally and electronically on a single silicon terrace (rendering obsolete the contribution from step edges in measured microscopic surface state conductance) has not been reported yet.

2.EXPERIMENTALS

The required dry hydrogenation procedure has been described in details elsewhere (reference 5). Local extraction of hydrogen atoms was carried out by the use of a commercial ultra-high vacuum scanning tunneling microscope device (JEOL STM/AFM 4500-XT) comprising an image observation chamber (including an AFM stage unit, a specimen parking mechanism and an optical microscope) attached to a treatment/analysis chamber equipped with specific transport mechanisms for the introduction of specimens holder bases and cantilever cassettes via a magnetic load-lock system.

Pre-determined bias (8 V, sample positive) and tunneling current (6 nA) were applied between a tungsten (W) tip apex and hydrogenated silicon surface areas during scanning nanometer-sized linear shapes at room temperature. Each lithography event was followed by tunneling measurements in constant current topographic (CCT) mode for an immediate resolution of artificial structures. Our choice of a feedback controlled dehydrogenation method originated from the particular interest to arrange silicon nanowires in serial sequences, leading to a novel original pattern representing a promising basis for the realization of future SET organic nanodevices. Prior to selective dehydrogenation, electrochemically etched STM tips (2N NaOH solution) were cleaned by baking cycles *in situ* and the successive application of voltage pulses (-6 V<sample bias<-10 V). Initial scans were performed with tunneling parameters set to the related lithography mode in order to confirm a non degradation of the apex before entailing selective extraction of hydrogen atoms.

Pre-selected on-oriented Si(111) specimens (1000 Ω.cm<ρ<1500 Ω.cm-1x7 mm^{2}x450 μm) were degreased in organic solutions (acetone, ethanol) and inserted a conventional way in UHV. Their cleaning procedure consisted of a lengthy outgassing period at ~500°C, followed by high temperature annealing steps up to ~1100°C under a very low vacuum pressure ($P<5.10^{-8}$ Pa). For final preparation, the silicon surface was flashed at ~1200°C (t<10 s), stabilized at ~800°C (t~1 min.) and slowly cooled down to RT (t~20 min.), giving rise to non defected 7x7 dimer-adatom-stacking-fault (DAS) structures chemically suitable for dry hydrogenation. The application of an high hydrogen dose (1.08 Pa.s) ensures the final presence of Si(111):1x1:H structures in the restatom layer at room temperature. Several monolayers (1ML: 7.84x10^{14} atoms/cm^2) of lead (Pb) material were deposited from a Knudsen cell onto hydrogen passivated and depassivated regions. Thermal desorption of metal at high temperature was subsequently processed until final resolution of stable atomically defined lead nanostructures confined on a single silicon terrace. Features sizes and shapes are controllable and can be modified for further realizations of elaborated nano-scale circuits on Si(111):H templates. The surrounding of group IV nanolines by unreactive passivated regions promotes ideal electron transport measurements with the four point probe method.

3.RESULTS AND DISCUSSION

3.1 Fabrication of atomic-scale lead nanostructures

Hydrogenation and tip-induced selective depassivation: prior to STM-patterning *in situ*, the Si(111) sample surface was hydrogenated by direct exposure of 7x7 DAS structural features (e.g. adatoms, restatoms, corner holes and dimer walls) to thermally activated hydrogen atoms (T>1800 K). Bare silicon nanometer-sized areas were fabricated on the hydrogen-passivated material by tip-induced selective extraction of hydrogen atoms for pre-determined lithography conditions: 8 V (sample positive), 6 nA.

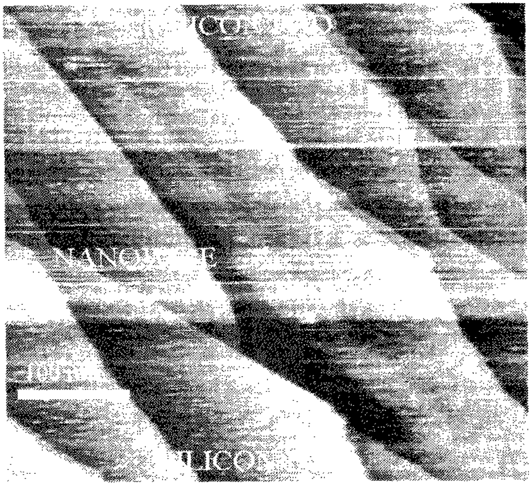

Fig.1 STM image of the original silicon nanowire isolated on a narrow single terrace (sample bias : 1.5 V and tunnel current : 0.5 nA). Bright horizontal lines are attributed to tip instability induced by residual noise occuring during the measurements .

Figure 1 shows a series of initial STM scans performed on a silicon nanowire which was confined on a single hydrogenated (111) terrace of ~200 nm width. The quasi-linear shape appears brighter than surrounding hydrogenated regions, due to the presence of chemically active silicon dangling bonds. The overall feature extends beyond ~700 nm length for few tenths nanometers width, and consist of three sub-regions which regarding extremities intersect each other for the final realization of a nanoline (3x~230 nm). Two silicon pads of 1x10^4 nm^2 superficy each were fabricated in a similar way, i.e. by selective extraction of hydrogen atoms, at both ends of the nanowire. They were designed in such specific lateral positions in order to permit a further recognition of the entire pattern by CCT imaging, once lead evaporated onto and thermally desorbed from.

Lead evaporation and STM-monitored desorption: in situ condensation of group IV atoms was subsequently processed onto patterned silicon regions by the molecular beam epitaxy (MBE) technique. The deposition of metal atoms was found to form tri-dimensional clusters, confirming a Volmer-Weber growth mode previously characterized on hydrogen-passivated Si(111) surfaces [7]. High temperature desorption of sole Pb atoms at T~400°C (reference 7) from both hydrogenated and dehydrogenated areas was STM-monitored by successive acquisition of CCT data until the resolution of atomically defined nanostructures inside depassivated regions (cf Fig. 2).

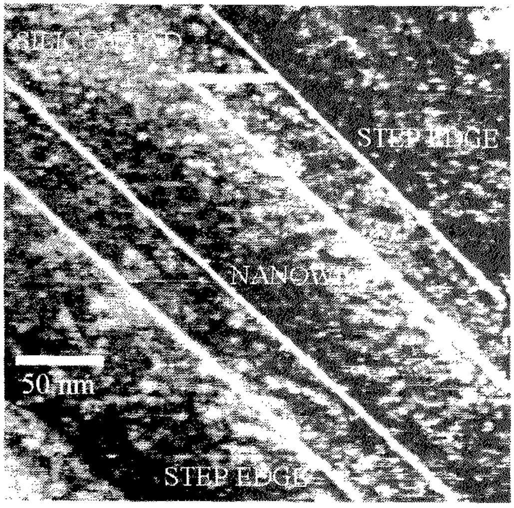

Fig.2 Left side of the depassivated area after MBE deposition and thermal desorption of lead at 400^{0}C for 1min. Imaging conditions: 2 V (sample positive), 1 nA.

3.2 Characterization of confined lead nanostructures:

STM structural study: Figure 3 shows a brow up of a local area selected in the central part of the metal-covered nanowire. Parallel ridges attributed to the presence of lead material are visible, extending longitudinally along a direction rotated 60° from [1-1 0], the step edge direction in Fig. 2. Hence, bright dots in apparent random distribution visible in Figs. 2 and 3 can reasonably be interpreted as intrinsic disorder-related lead atomic structures tilted from their original positions, (originating significant changes in local surface charge density), forcing the probing tip to retract in order to keep a constant demanded tunneling current. The near proximity of topographical boundaries with surrounding hydrogen-passivated regions located in higher atomic layers may be responsible for residual strain actually compensated by local tilt along the ridges structures.

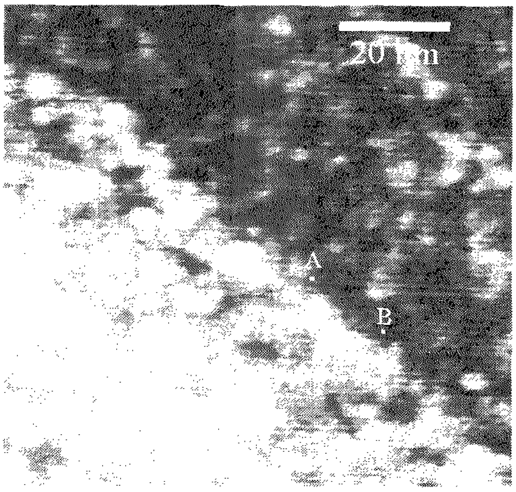

Fig.3 Atomic resolution of a typical boundary region between hydrogen-passivated (dark) and metal-covered areas (bright). Visible ridges extend longitudinally along the image diagonal with a lateral spacing of 2 nm. Imaging conditions: 2 V, 1 nA.

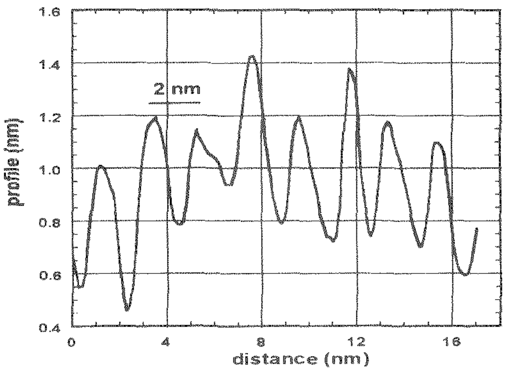

Fig.4 A-B cross-sectional profile of Pb ridges. Peaks are found to range in several nanometers distances due to the local tilt originated by residual strain induced from the structural confinement.

Our detailed STM structural investigations at higher resolution confirmed the non capability of the ridges to translate in transverse direction in respect with the underlying substrate. Our reported lateral spacing of 2 nm, which is about three times that of π-bonded chains periodicity (0.67 nm) on a Si(111) 2x1 reconstructed surface, eradicates the latter superstructures as possible supporting blocks. However, if considering our lithography conditions, one can easily assume that the original nanowire is initially composed of 2x1 π-bonded silicon chains. Pseudo-potential energy calculations conducted by Northrup and Cohen nearly two decades ago, showed that a 2x1 π-bonded silicon surface can result from an ideal 1x1 bonding topology by slightly increasing the total surface energy of 0.03 eV per surface atom [8]. We believe that the initial condensation of Pb atoms by the molecular beam epitaxy technique (MBE) has led to the saturation of empty silicon dangling bonds sites inside depassivated regions, forcing the original surface structure to reconstruct in an ideal bonding topology due to the sudden increase in total energy. As a matter of fact, a Si(111) restatom layer may obviously represent a concrete structural support for lead ridges. Figure 5 shows an atomic model presented for the better comprehension of protruding metal ridges. In this model, Pb atoms sit on an unreconstructed topmost silicon layer in T_4 adsorption sites, which positions are similar to the ones occupied by group IV atoms for the final formation of a Si(111) $\sqrt{3}x\sqrt{3}$-β phase with an associated saturation coverage of 1/3 ML. The remaining electron residing in a vertical p-type orbital for each Pb atom may participate in chemical bonding with nearest-neighbours, leading to the formation of uni-dimensional σ-bonds stabilizing the metal-covered silicon regions. A closer inspection of corresponding ridges features brings in fact an estimated width of ~1nm for a lateral spacing of 2 nm, confirming that only three out of five adjacent rows of bonded Pb atoms are distinguishable in our imaging conditions. The ridges features evidenced by STM imaging certainly traduce a significant enhancement of surface charge density due to a particular bonding configuration inside periodical arrangements of three nearest neighbouring "chains" of Pb atoms. In the case of parallel arrangement of Pb ad-dimers, one may expect the surface electronic structure to be dominated by the signatures of two occupied surface state bands under the Fermi level, similar to ones encountered on a Si(100) 2x1 surface. We consider in fact, the possibility for Pb ad-dimers to buckle at room temperature and to originate charge transfer towards a single atom. The related surface electronical status can thus be assimilated to the one induced by buckled silicon dimers on a Si(100) pristine surface at RT. Initial energy dispersions of both ridges valence surface states may consequently closely resemble those exhibited by filled dangling bonds of upper atoms in asymmetric dimers and by adatom backbonds, representing the principal building bloks of a Si(100) 2x1 reconstructed surface.

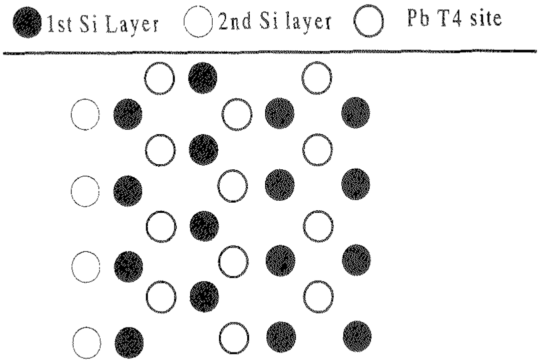

Fig.5 Our atomic model for the new lead phase. Three parallel rows of T_4 sites are represented, extending laterally over ~12 Å distance.

4. CONCLUSIVE REMARKS

Atomically defined nanometer-sized lead ridges confined on a single hydrogenated Si(111) terrace were fabricated for the first time by the use of a scanning tunneling microscope in ultra-high vacuum. A detailed analysis of ridges structural and electronical features suggests a strengthened bonding configuration between dimerized Pb atoms and a supporting unreconstructed Si(111) restatom layer.

Acknowledgements

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