



## The electronic properties of Co nanowires on Cu(110)-p(2×3)N

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### ABSTRACT

We present the first measurements of the differential conductance of Co wires grown on top of Cu(110)-p(2×3)N (Cu<sub>3</sub>N). We apply scanning tunneling spectroscopy (STS) in constant height and constant current mode to access the electronic density of states of the sample over a wide energy range. All measurements have been performed at 7K. Our study reveals that the differential conductance of the Co wires is very similar to that of Cu<sub>3</sub>N. Spectra of the differential conductance measured on the Co wires and on Cu<sub>3</sub>N reveal that both systems exhibit the same characteristic features near +1.8V and +3.5V.

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### 1. Introduction

To study and characterize the peculiar electronic and magnetic properties of individual nanostructures or even single atoms, it was demonstrated recently that Cu<sub>2</sub>N on Cu(100) [1,2] can act as a useful intermediate layer. The authors [1] find that Cu<sub>2</sub>N on Cu(100) strongly suppresses the high density of states of Cu(100) around the Fermi energy. Here we investigate the related system Cu(110)-p(2×3)N (Cu<sub>3</sub>N on Cu(110)) [3–5]. This system is especially interesting, since it promotes the growth of extended nm wide quasi one-dimensional nanowires of numerous metals [6,7]. Such nanowires are thought to play an important role in future nanoscale electronic devices. However, the electronic properties of the nanowires grown on Cu<sub>3</sub>N have not been revealed before, and they are studied here.

We use a Cu(110) single crystal as a substrate for our experiments. We investigate the morphology and electronic properties of the sample by scanning tunneling microscopy (STM) and spectroscopy (STS) at 7K. The surface of the Cu(110) crystal is cleaned under ultra high vacuum conditions (<5×10<sup>-11</sup> mbar), by cycles of ion bombardment (Ar<sup>+</sup>, 2×10<sup>-7</sup> mbar, 1keV, dose 1.40mC/cm<sup>2</sup>, normal incidence) and subsequent annealing at 700K for 15 min. An atomically clean Cu(110) surface with atomically flat terraces is obtained (see Fig. 1(a)). The

nitrogen network on top of the Cu(110) surface is prepared by bombarding the surface with N<sup>+</sup> ions (2×10<sup>-7</sup> mbar, 600eV, 1.5 μA/cm<sup>2</sup>, normal incidence) for 30 min at a temperature of 550K. The successful preparation of the Cu<sub>3</sub>N network [7,5] is verified by STM, and its 2×3 unit cell is atomically resolved (see Fig. 1(b)). Upon deposition of Co at room temperature wire-like structures form on the surface via self assembly (see Fig. 3) [7]. The sample is immediately cooled down after Co deposition to minimize potential intermixing. The sample temperature reaches 100K after 1 h, and 7K after 8 h.

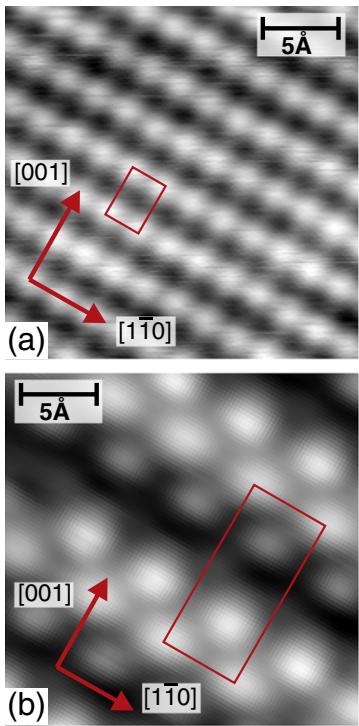
For spectroscopy, we measure the differential conductance  $dI/dV$  of the sample by modulating the gap voltage  $V_{\text{Gap}}$  with a small AC voltage and using phase sensitive detection of the modulation of the tunnel current  $I_T$  by a lock-in technique ( $f_{\text{mod}}=5\text{ kHz}$ ,  $V_{\text{mod}}=20\text{ mV}$ ).<sup>1</sup> The  $dI/dV(V_{\text{Gap}})$  signal is recorded either as a function of  $V_{\text{Gap}}$  or in the imaging mode as a function of position at a fixed  $V_{\text{Gap}}$ . In this work we utilize two different modes of spectroscopy. For the low voltage range ( $|V_{\text{Gap}}|<2\text{ V}$ ) we record spectra at constant tip-sample distance of approx. 0.5 nm (feedback loop of  $I_T$  switched off). To access electronic properties at higher voltages we record the  $dI/dV$  signal with varying tip-sample distance, i.e. at constant tunnel current (feedback loop of  $I_T$  switched on) [8]. The corresponding spectra are therefore denoted as  $dI/dV|_I$  spectra. In this mode the tip-sample distance  $Z$  increases by 0.7 nm when  $V_{\text{Gap}}$  reaches +5.0V.

Fig. 1 presents atomically resolved constant current STM images of the clean Cu(110) surface and the nitrogen network grown on top of

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<sup>1</sup> The bias voltage  $V_{\text{Gap}}$  is applied to the sample.



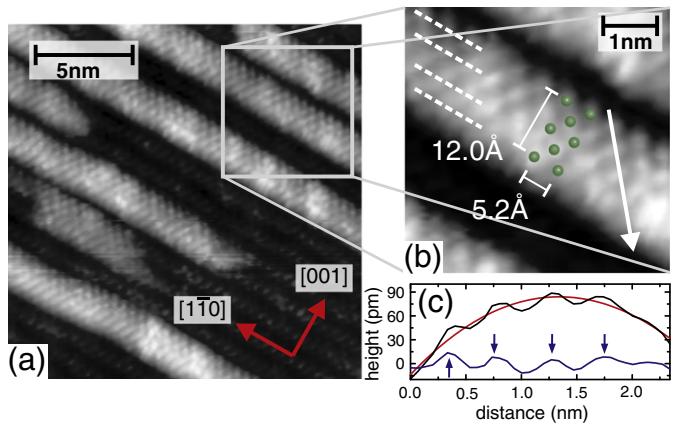
**Fig. 1.** Atomically resolved STM topography images of Cu(110) (a) and Cu<sub>3</sub>N (b). Red rectangles in (a) and (b) denote the 1×1 and 2×3 unit cells, respectively. Imaging conditions: (a)  $V_{Gap} = -0.02\text{ V}$ ,  $I_T = 20\text{ nA}$ , (b)  $V_{Gap} = +0.2\text{ V}$ ,  $I_T = 10\text{ nA}$ .

it. We extract the surface unit cell size of Cu(110) ( $0.255\text{ nm} \times 0.361\text{ nm}$ ) and Cu<sub>3</sub>N ( $0.502\text{ nm} \times 1.094\text{ nm}$ ) from our STM data, and find that the values agree with literature reference data [5,7,9]. The electronic properties of Cu<sub>3</sub>N have been investigated recently by Bhattacharjee and colleagues [5]. They find that  $dI/dV$  spectra obtained in constant height mode, i.e. with the feedback loop switched off, appear featureless except for an exponential increase of the signal above 4V. Our experimental data show the same characteristics, though we observe the exponential increase already around 2V, see inset of Fig. 3(e). We ascribe this to the different tunneling parameters applied here.

To study the electronic properties over an extended voltage range we have also recorded  $dI/dV|_{I_T}$  spectra on the Cu<sub>3</sub>N network (Fig. 3(e)). We did not observe any significant features in the Cu(110) spectrum at negative bias. Therefore we focus on the positive voltage range here. In our experiments we have routinely observed two pronounced peaks at +1.8V and +3.3V (Fig. 3(e)). We attribute both peaks to the electronic structure of the Cu<sub>3</sub>N surface [5,10]. The electronic properties of Cu<sub>3</sub>N are discussed in detail in Ref. [5].

Co deposition on Cu<sub>3</sub>N leads to the formation of nanowires as depicted by the constant current STM image displayed in Figs. 2 and 3(a). The Co wires form in the troughs of the Cu<sub>3</sub>N surface and have a minimum separation between the centers of two adjacent wires of 2.2 nm [7]. Details of the atomic structure of the Co wires are revealed by constant current STM images in Fig. 2. The wires grow in the [110] direction of the Cu(110) surface and we have obtained atomic resolution on all wires imaged in (a). Our atomically resolved topography images confirm the main characteristics of the structural model of Ref. [7].

To reveal details of the electronic structure of Co wires grown on Cu<sub>3</sub>N we record  $dI/dV$  maps and  $dI/dV|_{I_T}$  spectra on the wires. The results are presented in Fig. 3. Fig. 3(b)–(d) shows  $dI/dV$  images of the area marked by a white rectangle in (a) measured at different bias voltages. We find that the contrast between the Co wires and the substrate is changing with bias voltage. At certain voltages the wires appear



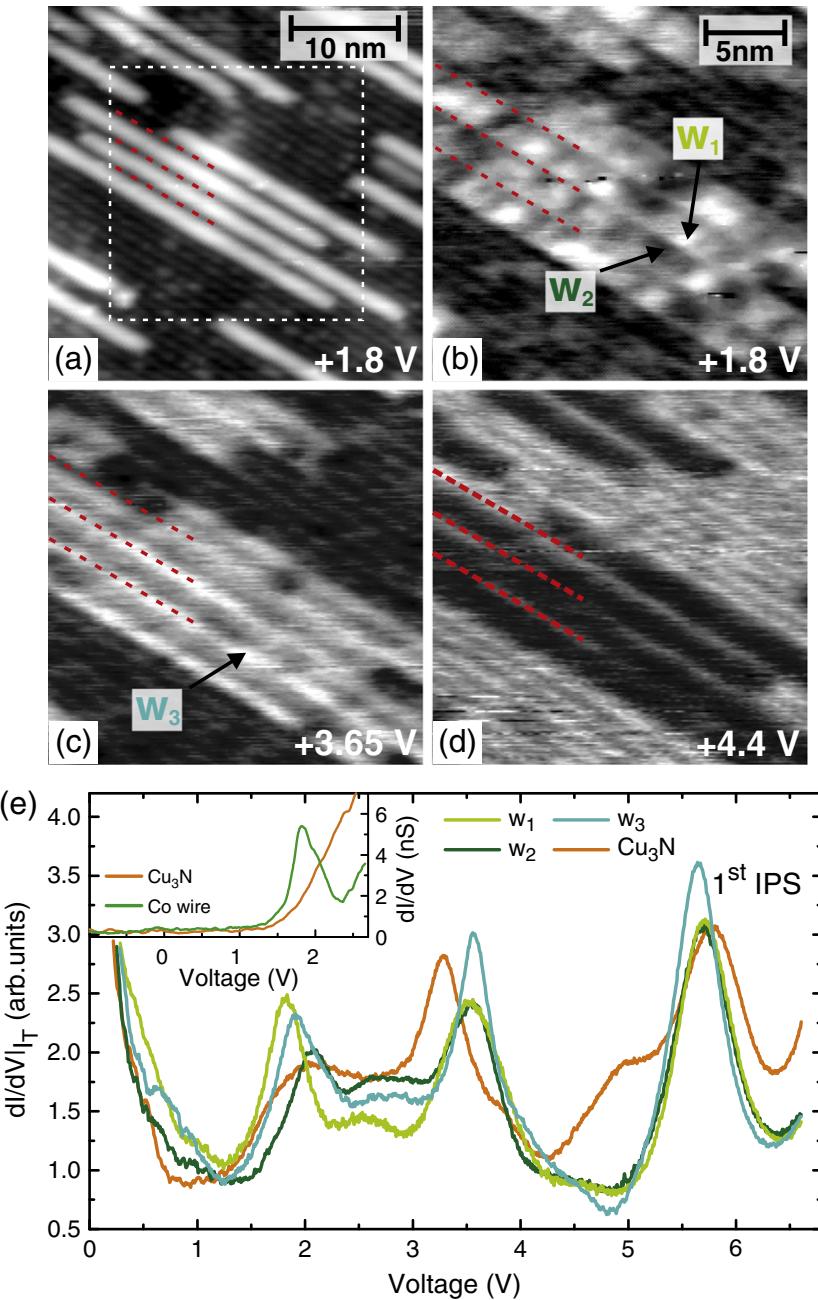
**Fig. 2.** Atomically resolved constant current STM images of Co wires grown on top of Cu<sub>3</sub>N. (a) Co forms elongated wire-like structures in the troughs of the Cu<sub>3</sub>N substrate. Imaging conditions:  $V_{Gap} = -0.2\text{ V}$ ,  $I_T = 3.0\text{ nA}$ . (b) Zoom-in of (a). Green circles mark atom positions according to the model of [7], dashed lines indicate lines of atoms. (c) Line scan along the white arrow in (b), where arrows mark positions of Co atoms. The red curve is a polynomial fit through the raw data (black) and was used to remove the curvature from the line scan (blue).

brighter than the substrate and at other energies the opposite contrast is observed. A close inspection of Fig. 3(b) reveals that at +1.8V the  $dI/dV$  signal within the Co wires shows pronounced spatial variations. These variations are irregular and do not show any periodic behavior. Possible mechanisms causing these inhomogeneities are discussed below. Another remarkable observation is that in Fig. 3(b) and (c) the  $dI/dV$  signature of the wires extends farther than the width of the wires, which is deduced from topography. The topography shows well separated wires with a small gap between two neighboring structures (red dashed lines). However, spectroscopy images at +1.8V and +3.65V do not reveal a distinct gap between adjacent wires. Only at +4.4V(d) the wires appear well separated again. A most peculiar behavior of the  $dI/dV$  signal is visible from data presented in (c). Here the  $dI/dV$  signal has a maximum at the very edge of the wires and a minimum in the center. For adjacent wires the width of the  $dI/dV$  maximum at the rim of the wires corresponds precisely to the width of the gap between them.

To investigate the  $dI/dV$  inhomogeneities within the wires in more detail, we measure single point spectra on a “bright” ( $w_1$ ) and on a “dark” ( $w_2$ ) spot, and between the wires ( $w_3$ ). The results are displayed in Fig. 3(e). A spectrum of the Cu<sub>3</sub>N substrate is shown for comparison. All spectra show a pronounced peak at +5.8V. This peak is a signature of the first image potential state (IPS), where the energy position is shifted due to the Stark effect caused by the electric field of the tip [11]. This assignment is corroborated by our observation that the energy position of the first IPS depends on  $I_T$  [12,13]. We use this property to distinguish IPS from other electronic features in the spectra.

All three Co spectra show two peaks below the first IPS at +5.8V. The position of the first peak changes from +1.8V at the bright spot to +1.9V between the wires, and it reaches +2.2V at the dark spot. The intensity of the peak decreases with the shift to higher energies. The second peak, however, does not change its energy position and shows the same intensity for spectra  $w_1$  and  $w_2$  taken on the wire. Only spectrum  $w_3$  taken at the gap position shows an increased intensity, which is in line with the data shown in Fig. 3(c).

A possible reason for the inhomogeneous  $dI/dV$  signal within the Co wires are structural imperfections. A close inspection of Fig. 2 reveals that the wires indeed exhibit noticeable structural inhomogeneities. The wires are not perfectly straight on a length scale of 5–10 nm. Some spots within the wires exhibit an increased apparent height. These effects could be ascribed to structural and/or chemical defects or to relaxation effects. In view of previous work on mesoscopic



**Fig. 3.** Co wires grown on Cu<sub>3</sub>N. All images show the same sample area and dashed lines mark identical positions. (a) STM constant current overview image. (b)–(d)  $dI/dV$  maps obtained at the denoted voltages. The  $dI/dV$  signal changes considerably as a function of voltage and position within the wire ( $I_T=0.5\text{ nA}$ ). (e)  $dI/dV|_{I_T}$  spectra obtained at the positions marked in (b) and (c). Initial tip sample distance is set by  $V_{\text{Gap}}=+1.8\text{ V}$ ,  $I_T=0.5\text{ nA}$ . The inset shows  $dI/dV$  spectra obtained with deactivated feedback loop. A pronounced peak around  $+1.8\text{ V}$  is found in the spectrum of the Co wires measured at the center of the wires. Tip stabilization parameters:  $V_{\text{Gap}}=-2.0\text{ V}$ ,  $I_T=1.0\text{ nA}$ .

relaxation [14], we propose that structural inhomogeneities caused by relaxation effects could possibly lead to the shift of the first peak observed in Fig. 3(e).

A comparison of the Co spectra w<sub>1</sub>, w<sub>2</sub> and w<sub>3</sub> with the Cu<sub>3</sub>N spectrum in Fig. 3(e) reveals a striking similarity of the main features. The spectra exhibit peaks positioned near  $+1.8\text{ V}$  and  $+3.5\text{ V}$ . This similarity comes as a surprise since it suggests that Cu<sub>3</sub>N and Co grown on top have similar electronic properties. Despite the similar spectral features of the  $dI/dV|_{I_T}$  spectroscopy, we also observe two significant differences in the electronic properties of Co wires and Cu<sub>3</sub>N. These differences show up in  $dI/dV$  spectra recorded in constant height mode (cf. inset Fig. 3(e)). First, the  $dI/dV$  spectrum of Co shows a peak around  $+1.8\text{ V}$ , whereas the Cu<sub>3</sub>N spectrum shows a monotonic increase in this energy

range. Second, the peak at  $+1.8\text{ V}$  in the  $dI/dV|_{I_T}$  spectrum of Co depends on the position w<sub>i</sub> within the wire, whereas the peak position in the Cu<sub>3</sub>N spectrum does not depend on the bonding site N<sub>i</sub> [5].

From these observations we conclude that the peak near  $+1.8\text{ V}$  is strongly affected by the presence of Co on the surface. We speculate that this peak is the signature of a surface resonance caused by the hybridization between Co and Cu<sub>3</sub>N electronic states. For the second peak near  $+3.6\text{ V}$  the hybridization seems to be more dominant, since the peak position does not depend on the measurement position w<sub>i</sub>. We think that the states leading to this peak are strongly dominated by the electronic structure of Cu<sub>3</sub>N itself. Choi and coworkers [15] have observed very similar features in  $dI/dV|_{I_T}$  spectra measured on c(2×2)N-Cu(100) (Cu<sub>2</sub>N). They report two peaks, one at  $+2.2\text{ V}$

and one at +3.8 V, very similar to the features that we observe on Cu<sub>3</sub>N. Hence, we propose that the peaks reported here are closely related to electronic states of nitrogen.

In summary, the similarity of the spectroscopic features measured on Co/Cu<sub>3</sub>N and on Cu<sub>3</sub>N as plotted in Fig. 3(e) is striking. This suggests similar electronic properties of both systems. The corrugation of the nitride network offers many different adsorption geometries on a single substrate with correspondingly varying electronic environments. Further experiments on single atom spectroscopy need to be performed to investigate the interplay between bonding site and electronic properties. With this promising perspective in mind future input from theory could provide a detailed understanding of the electronic structure of Cu<sub>3</sub>N [7,16]. However, due to the complex geometrical structure of the Cu<sub>3</sub>N network this goal is a true challenge for state-of-the-art *ab initio* calculations.

## References

- [1] C.D. Ruggiero, T. Choi, J.A. Gupta, Appl. Phys. Lett. 91 (2007) 253106.
- [2] C.D. Ruggiero, M. Badal, T. Choi, D. Gohlke, D. Stroud, J.A. Gupta, Phys. Rev. B 83 (2011) 245430.
- [3] F.M. Leibsle, R. Davis, A.W. Robinson, Phys. Rev. B 47 (1993) 10052.
- [4] F.M. Leibsle, R. Davis, A.W. Robinson, Phys. Rev. B 49 (1994) 8290.
- [5] K. Bhattacharjee, X.-D. Ma, Y. Zhang, M. Przybylski, J. Kirschner, Surf. Sci. 606 (2012) 652.
- [6] X.D. Ma, T. Nakagawa, Y. Takagi, M. Przybylski, F.M. Leibsle, T. Yokoyama, Phys. Rev. B 78 (2008) 104420.
- [7] X.D. Ma, D.I. Bazhanov, O. Fruchart, F. Yildiz, T. Yokoyama, M. Przybylski, V.S. Stepanyuk, W. Hergert, J. Kirschner, Phys. Rev. Lett. 102 (2009) 205503.
- [8] G. Binnig, K.H. Frank, H. Fuchs, N. Garcia, B. Reihl, H. Rohrer, F. Salvan, A.R. Williams, Phys. Rev. Lett. 55 (1985) 991.
- [9] C. Kittel, Introduction to Solid State Physics, 8th ed. Wiley, Hoboken, NJ, 2005.
- [10] M. Passoni, F. Donati, A. Li Bassi, C.S. Casari, C.E. Bottani, Phys. Rev. B 79 (2009) 045404.
- [11] E.V. Chulkov, A.G. Borisov, J.P. Gauyacq, D. Sanchez-Portal, V.M. Silkin, V.P. Zhukov, P.M. Echenique, Chem. Rev. 106 (2006) 4160.
- [12] D.B. Dougherty, P. MakSYMovich, J. Lee, M. Feng, H. Petek, J.J.T. Yates, Phys. Rev. B 76 (2007) 125428.
- [13] We note that the precise term is Stark-shifted image-potential-derived states, see Ref. 10. For simplicity we stick to the term IPS.
- [14] M.V. Rastei, B. Heinrich, L. Limot, P.A. Ignatiev, V.S. Stepanyuk, P. Bruno, J.P. Bucher, Phys. Rev. Lett. 99 (2007) 246102.
- [15] T. Choi, C.D. Ruggiero, J.A. Gupta, J. Vac. Sci. Technol. B 27 (2009) 887.
- [16] A. Soon, L. Wong, B. Delley, C. Stampfl, Phys. Rev. B 77 (2008) 125423.