

SUPPORTING INFORMATION

FOR THE PAPER

Highly sensitive detection of TCNE on chemically passivated silicon-on-insulator

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Contents:

1. Physical properties of TCNE
2. Surface characterization studies of TCNE adsorption on silicon
 - 2.1 Vapour phase adsorption of TCNE studied by ATR-FTIR
 - 2.2 Reactivity of Si(100)-H with TCNE studied by HREELS
 - 2.3 Liquid phase adsorption of TCNE studied by ATR-FTIR
3. References

1. Physical properties of TCNE

Purum grade (98%) tetracyanoethylene (TCNE); white crystalline solid; C₆N₄; FW 128.09; mp 198 °C, from Sigma-Aldrich was stored at 4 °C, then warmed to room temperature for use. ¹³C NMR was used to confirm the impurities (mostly water) are in the 1% range. *Caution: Very Toxic.* TCNE slowly evolves hydrogen cyanide (HCN) in moist air at room temperature [1]. It should be handled with appropriate protective equipment, including a full-face particle respirator type N100 (US). Consult a material safety data sheet before (MSDS) use.

The large electron affinity of this conjugated species arises from the low electron density around the central alkene, resultant from the four surrounding electronegative cyanide (CN) groups. Many important properties are listed below in Table S1. The most relevant scientific work including basic properties, chemical reactivity and charge transfer complexes of TCNE can be found in detail in the following reviews and articles [2-4]:

[2] The Chemistry of Tetracyanoethylene:

Dhar, D. N. *Chem. Rev.* **1967**, *67*, 611.

[3] Tetracyanoethylene (TCNE): The Characteristic Geometries and Vibrational Absorptions of Its Numerous Structures:

Miller, J.S. *Agnew. Chem. Int. Ed.* **2006**, *45*, 2508.

[4] Charge and momentum densities of cubic tetracyanoethylene and its insertion compounds:

Bélemlilga, D.; Gillet, J.M.; Becker, P.J. *Acta Cryst. B.* **1999**, *55*, 192.

Table S1: Important physical properties of tetracyanoethylene and their date(s) of findings.

Property	Assignment	Reference (s)
synthesis	1957	Cairns <i>et al.</i> , 1957 [1]
		Cairns <i>et al.</i> , 1958 [5]
		Heckert & Little., 1957 [6]
electron affinity	3.17±0.20 eV	Chowdhury & Kebarle, 1986 [7]
enthalpy of sublimation	18.65 kcal/mol	Looney & Downing, 1958 [8]
vapour pressure at 20°C	2x10 ⁻³ Torr	Boyd, 1963 [9]
crystal structure	monoclinic and cubic	Bekoe & Trueblood, 1960 [10]
HOMO-LUMO gap	10.3 eV	Bélemlilga <i>et al.</i> , 1999 [4]

2. Surface characterization studies of TCNE adsorption on silicon

To account for the partial reversibility in the electrical measurements on SOI-H (Figure 2a), spontaneous reactions of TCNE itself and/or accelerated oxidation of the H-terminated surface in air were initially suspected. However both of these possibilities were not observed to any appreciable degree (and at much higher exposure levels than used in the electrical measurements) at room temperature, as outlined below.

2.1 Vapour phase adsorption of TCNE studied by ATR-FTIR

As discussed in the text, ATR-FTIR (Figure 3a) reveals successive exposure of TCNE on Si(100)-H leads to a broad absorbance band from 2180-2260 cm^{-1} , with a distinct stretch centered at 2220 cm^{-1} and weaker shoulder at 2195 cm^{-1} . These features overlap with the range of nitrile group stretch frequencies known for various TCNE complexes [3], thereby suggestive of some residual coverage of TCNE that does not desorb effectively at room temperature. Additionally, the weak shoulder at 2195 cm^{-1} falls within the acceptable range for an anionic species TCNE^- , although assignment of this peak remains inconclusive. The features observed in this range, on their own, are somewhat problematic to clearly distinguish bound TCNE modes from oxidation, (either by ambient or induced by exposure) without controls. The complication arises since Si(100)-H is also known to gradually exhibit broad peaks at 2200 cm^{-1} and 2250 cm^{-1} after several hours in ambient, attributed to bonding configurations $\text{SiH}_2(\text{O}_2)$ and $\text{SiH}(\text{O}_3)$, respectively [11]. The first control experiment was to measure the spectrum of the H-terminated surface left in ambient atmosphere over time without exposure to TCNE as shown in Figure S1a.

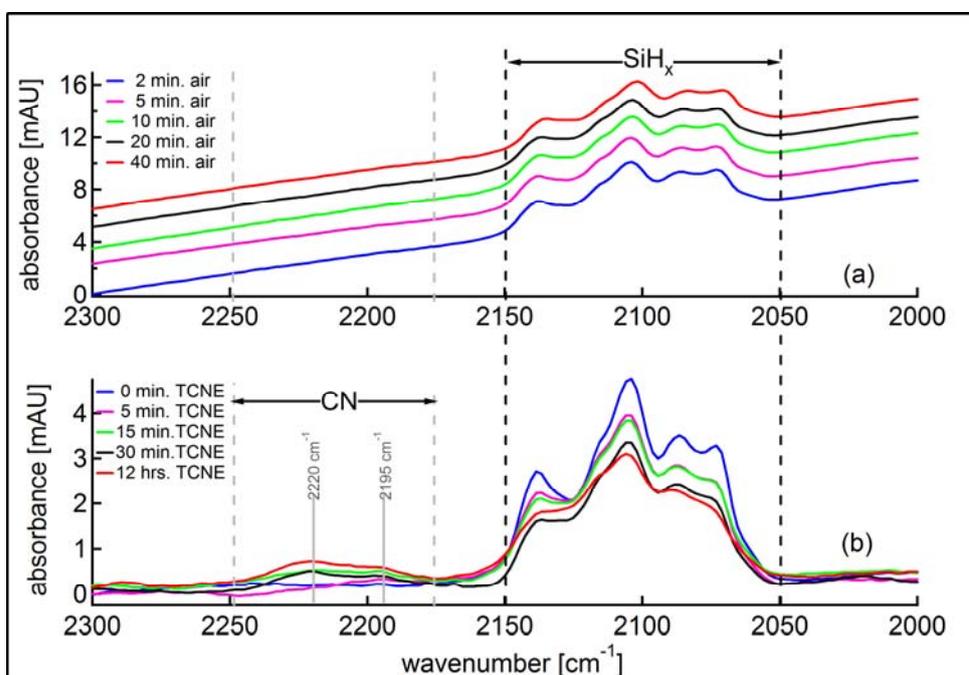


Figure S1: ATR-FTIR control experiments comparing spectra in air before and after TCNE exposure. (a) The H-Terminated surface, left in air for up to 40 min. shows no measurable absorbance attenuation in the SiH_x stretching region, and there are no observable oxidation peaks as reported by Niwano *et al.* in this time frame. (b) Upon successive exposure to TCNE the spectra begin to show broad absorbance consistent with

the CN stretching modes of TCNE's nitrile groups, with distinct peaks at 2220 and 2195 cm^{-1} .

The spectra are clearly unchanged after 40 min. ambient exposure, with no measurable attenuation or broadening of the SiH_x bands or observation of oxygen in the backbonds based on the peaks reported by Niwano *et al.* Only after exposure to TCNE do the spectra change in Figure S1b, revealing growth of broad features and the same distinct peaks in the CN stretching region, as well as intensity loss in the SiH_x stretching region. These observations support that the ambient vapour phase exposure onto H-terminated silicon leads to a measurable coverage of surface bound TCNE. However, it does not reveal the type of bonding to the surface, and does not preclude the possibility of indirectly observing oxidation induced by the TCNE. An experiment described in the next section using HREELS was able to address both these issues simultaneously.

2.2 Reactivity of Si(100)-H with TCNE studied by HREELS

Additional surface vibrational characterization using High Resolution Electron Energy Loss spectroscopy (HREELS) in ultrahigh vacuum (UHV) was done to complement the infrared results, which alone are insufficient to distinguish between oxidation and/or a chemisorbed versus a strongly physisorbed species. Loss spectra shown below in Figure S2 were recorded with an LK3000 spectrometer (specular at 60° , incident beam energy 6eV, resolution 32 cm^{-1}).

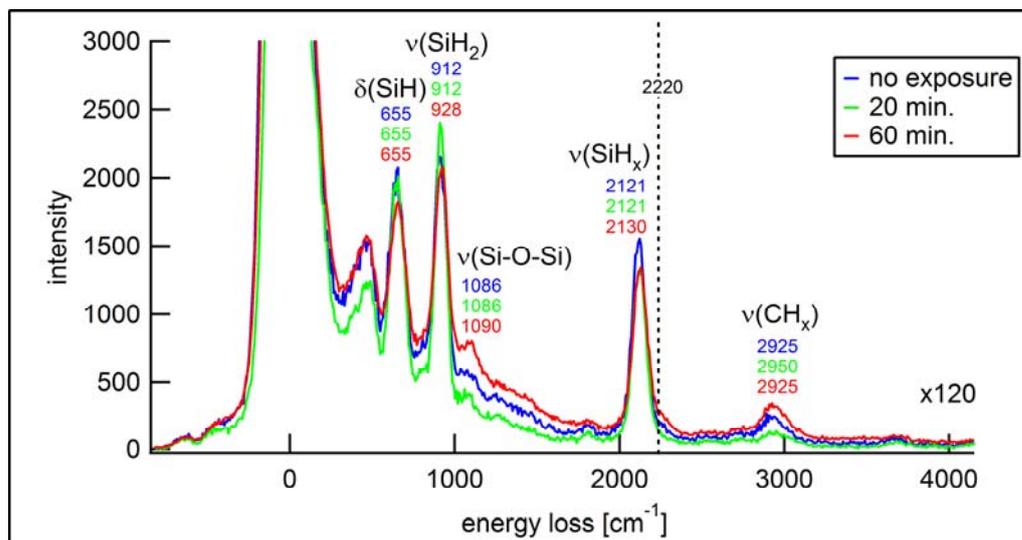


Figure S2: HREELS spectra of the freshly etched Si(100)-H surface and after exposure to TCNE (in air) for 20 and 60 minutes.

The sample was vented back to ambient atmosphere for exposure to TCNE, to be consistent with the environmental conditions used in the electrical measurements. To ensure an adequate dosage (in excess), exposure times of 20 and 60 min. were chosen, considerably longer than required to modulate the conductivity on SOI (seconds). The spectrum of the oxide-free freshly etched Si(100)-H does not change appreciably, even after 60 min. exposure to TCNE in ambient. The dominant features labeled in Figure S2

are the SiH_x stretch region (2121 cm⁻¹), the SiH₂ dihydride scissor mode (912 cm⁻¹) and the SiH bend mode (655 cm⁻¹). There is a small degree of hydrocarbon around 2925 cm⁻¹ and initially very little oxygen adsorbed in Si-O-Si backbonds (1086 cm⁻¹). After 60 min., the Si-O-Si stretch increases only slightly and the SiH stretch shifts to higher frequency, both of which are most likely caused by ambient exposure within this timeframe.

Preservation of the dominant silicon-hydrogen modes and absence of any appreciable level of oxidation in HREELS favours the assignment of the IR features in the region 2180-2260 cm⁻¹ (Figure 3a) more conclusively toward surface bound TCNE as opposed to modes involving oxygen. Furthermore, the CN bands visible in ATR-FTIR (ambient) are barely observable in HREELS (UHV). This observation supports a minimal coverage of TCNE, in the submonolayer range.

2.3 Liquid phase adsorption of TCNE studied by ATR-FTIR

Intentional deposition of TCNE from solution onto NaBr and various silicon surfaces Si(100)-X, where X=SiO₂ (chemical oxide), H, **C10** was carried out for comparison with the vapour phase IR observations. 135 ppm TCNE dissolved in acetonitrile (MeCN) was drop coated (~20 μL) and allowed to evaporate onto the surfaces to form multilayers, observable by eye as thin film interference regions. Listed below in Table S2 are the observed CN stretch positions. The relative intensities are qualitatively assigned in parenthesis according to: (s)-strong, (m)-medium, (w)-weak.

Table S2: Comparison of CN stretch modes of TCNE adsorbed on various surfaces by vapour and solution phase adsorption

sample	CN stretching vibration(s) [cm ⁻¹]	
	<i>vapour adsorption</i>	<i>solution deposition</i>
a. NaBr	-	2258(s), 2227(m), 2220 (m), 2189(w)
b. Si(100)/SiO ₂	-	2260(s), 2227 (m), 2212(w)
c. Si(100)-H	2220(m), 2195(w)	2258(s), 2220(m), 2212(w)
d. Si(100)- C10	none	none

Solid state measurements of uncharged, uncomplexed TCNE [C₂(CN)₄]⁰ on KBr are commonly reported to have two dominant C≡N infrared stretching vibrations, at approximately 2262 cm⁻¹(s) and 2228 cm⁻¹ (m) and a weaker mode at 2214 cm⁻¹(w) [3]. Our spectra on NaBr (transmission geometry) reproduce the two dominant IR modes as shown in Table S2-(a).

The above 3 modes reported were almost identically reproduced on a piranha cleaned chemical oxide with TCNE physisorbed from solution as shown in Table S2-(b). After 1hr in air the intensity in this region diminished significantly, suggesting that multilayers formed on the chemical oxide can desorb at room temperature. Upon rinsing in MeCN the CN modes completely disappeared, which is explained by the removal of residual TCNE by the solvent. These observations are illustrated below in Figure S3.

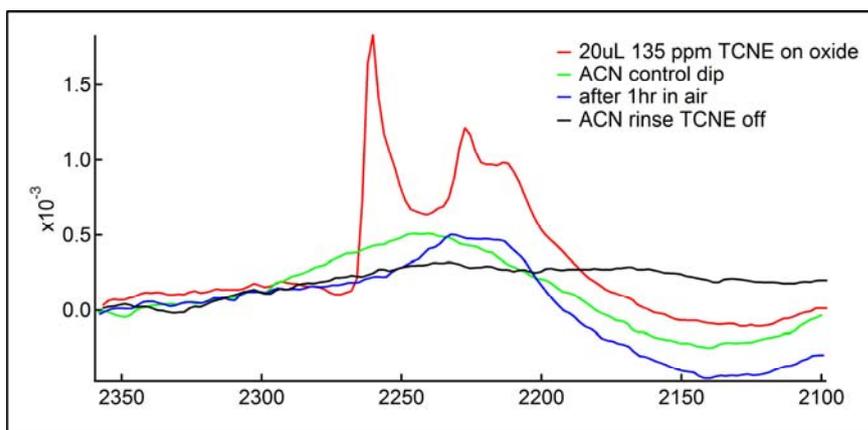


Figure S3: Deposition of TCNE from MeCN solution onto piranha treated chemical oxide studied by ATR-FTIR.

Solution phase deposition of TCNE onto Si(100)-H in Table S2-(c) shows a distinct mode at 2220 cm^{-1} , which was also observed in the vapour phase adsorption experiments, as discussed already in the text, and illustrated below in Figure S4. [Aside: However, we note the mode at 2258 cm^{-1} in Figure S3 is absent in the vapour phase adsorption (Figures S1, 3a). This may indicate, at low coverage, resulting from vapour adsorption, the mode at 2258 cm^{-1} , is not easily detected, or shifts to lower frequency resulting in the observed mode at 2220 cm^{-1} .] The CN absorbance in Figure S3 broadens slightly after 2 hours in air, but does not attenuate in intensity, as was observed for the chemical oxide, suggesting the TCNE is much more strongly bound to the H-terminated surface. Absorbance in this region could be partially reduced after rinsing in MeCN, further confirming that TCNE is more strongly bound on Si(100)-H compared to the chemical oxide.

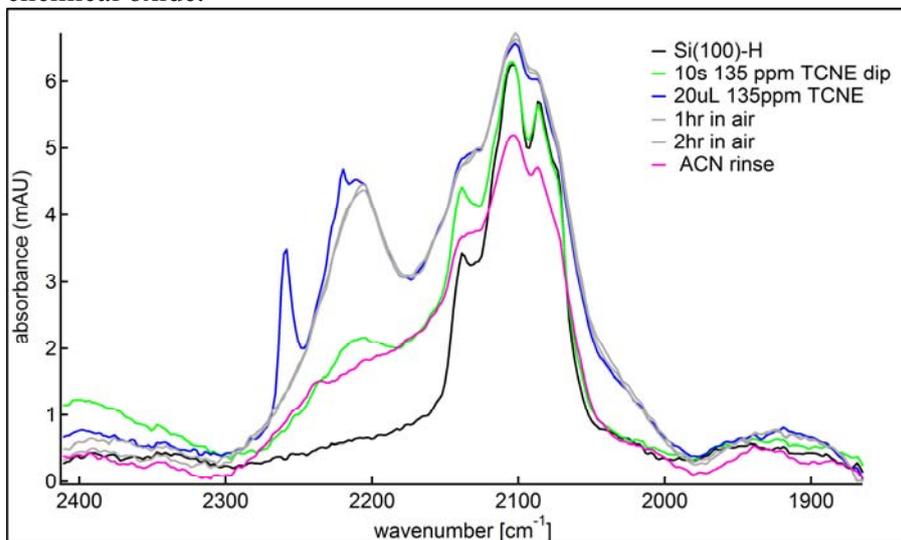


Figure S4: Deposition of TCNE from MeCN solution onto Si(100)-H studied by ATR-FTIR.

TCNE did not absorb to any measurable extent on Si(100)-C10 as shown in Table S2-(d), even after solution phase deposition. These observations are consistent with the

electrical measurements on SOI-C10, which show increased reversibility and reduced signal upon exposure to TCNE vapour, compared to SOI-H.

3. References

- [1] Cairns, T.L.; Carboni, R.A.; Coffman, D.D.; Engelhardt, V.A.; Heckert, R.E.; Little, E.L.; McGeer, E.G.; McKusick, B.C.; Middleton, W.J. *J. Am. Chem. Soc.* **1957**, *79*, 2340.
- [2] Dhar, D. N. *Chem. Rev.* **1967**, *67*, 611.
- [3] Miller, J.S. *Agnew. Chem. Int. Ed.* **2006**, *45*, 2508.
- [4] Bélemlilga, D.; Gillet, J.M.; Becker, P.J. *Acta Cryst. B.* **1999**, *55*, 192.
- [5] Cairns, T.L.; Carboni, R.A.; Coffman, D.D.; Engelhardt, V.A.; Heckert, R.E.; Little, E.L.; McGeer, E.G.; McKusick, B.C.; Middleton, W.J.; Scribner, R.M.; Theobald, C.W.; Winberg, H.E. *J. Am. Chem. Soc.* **1958**, *80*, 2775.
- [6] Heckert, R.E.; Little, E.L., Preparation of Tetracyanoethylene. U.S. Patent 2,794,823, June 4, 1957.
- [7] Chowdhury, S.; Kebarle, P. *J. Am. Chem. Soc.* **1986**, *108*, 5453.
- [8] Looney, C.E.; Downing, J.R. *J. Am. Chem. Soc.* **1958**, *80*, 2840.
- [9] Boyd, R.H. *J. Chem. Phys.*, **1963**, *38*, 2529.
- [10] Bekoe, D.A.; Trubelood, K.N. *Z. Crystallogr.*, **1960**, *113*, 1.
- [11] Niwano, M.; Kageyama, J.; Sawahata, J.; Miyamoto, N. *Surf. Sci. Lett.* **1994**, *301*, L245.