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Atmospheric Pressure Chemical Vapour Deposition of $NbSe_2$ Thin Films on Glass

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Atmospheric pressure chemical vapour deposition (APCVD) of niobium selenide films on glass substrates was achieved by reaction of di-*tert*-butyl selenide with $NbCl_5$ at 250–600 °C. X-ray diffraction showed that the $NbSe_2$ films were crystalline and of the $2H_a$ poly-type with cell constants close to those expected (a = 3.44 Å; c = 12.58 Å). Marked preferred orientation along either (101) or (200) was noted at higher deposition temperature and this unexpectedly varied depending on distance from the reactor inlet. The films produced at 600 °C showed exactly the Nb/Se ratio expected for $NbSe_2$ by energy dispersive analysis by X-rays. The films deposited at the substrate temperatures of 500 °C or less were selenium rich with a niobium to selenium ratio of 1:2.5. The films produced at 600 °C were dark-green, powdery and poorly adhesive. The films produced at 500 °C and below were dark-brown matte in appearance, they passed the Scotch tape test, but could be scratched with a steel scalpel. SEM showed that the films were composed of plate-like crystals, which become longer and thicker with increasing deposition temperature.

1. Introduction

Niobium diselenide ($NbSe_2$) is an important material because of its wide range of interesting physical properties, such as the presence of both a charge density wave transition and a superconducting transition. The structure of this low dimensionality layered material is hexagonal ($P6_{3/mmc}$) and composed of strongly bonded molecular layers stacked in a close-pack manner – with weak van der Waals interactions between the layers – which leads to highly anisotropic properties. Like all the layered group V transition-metal dichalcogenide, $NbSe_2$ has many different crystallographic poly-types, for example $2H_a$-, $2H_b$-, 3R-, $4H_a$-, $4H_{d1}$- and $4H_{d2}$-$NbSe_2$, depending on how the molecular layers stack-up and in turn the specific poly-type determines the physical properties of the materials. The poly-types $2H_a$- or $2H_b$-, and $4H_a$-$NbSe_2$ are superconducting with a transition temperature of T_c = 7.2 K and T_c = 6.3 K, respectively.[1,2] A charge-density wave is present in all the $NbSe_2$ polytypes. Moreover, an incommensurate charge-density wave is present in 2H-$NbSe_2$ below T_c = 33.3 K. Its structure remains incommensurate through the superconducting transition.[3] Even though the phase diagram of the niobium–selenium system is not fully known, many forms of niobium selenide, apart from $NbSe_2$, have been observed, such as Nb_5Se_4, Nb_3Se_4, $NbSe_2$, $NbSe_3$ and $NbSe_4$.[2,4–6]

Similar to most of the transition-metal dichalcogenides, $NbSe_2$ has been cited for use as an electrical conductor and as a solid lubricant at high temperature. $NbSe_2$ is also a good intercalation host. It has been shown that the growth of hydrogen intercalated in H_xNbSe_2 results in changes in the conductivity type from metallic to semiconducting.[7] Therefore, due to this sensitivity to intercalated molecules, niobium diselenide films may, as titanium diselenide films, find application as hosts for sensor materials.

The most common method to grow crystals of $NbSe_2$ is the vapour-phase-transport of prereacted polycrystalline $NbSe_2$ with iodine as a transport agent. $NbSe_2$ thin films have been grown using van der Waals epitaxy (VDWE) and pulsed-laser deposition (PLD).[7,8] To the best of our knowledge a CVD route to $NbSe_2$ has not been reported to date.

Here we present the CVD of $NbSe_2$ thin films. The motivation for this work was to produce niobium selenide films on glass and to use precursors other than H_2Se. One interesting feature of this work was the unexpected variation in preferred orientation that was noted depending on the position of analysis on the substrate.

2. Results and Discussion

Synthesis and Characterisation

Atmospheric pressure CVD reactions of $NbCl_5$ with tBu_2Se were studied on glass substrates at 250–650 °C. The deposition was observed on both top plate and substrate. The extent of the film coverage was dependent on the deposition temperature. Only the six first centimetres of the substrate were coated for a deposition temperature of 600 °C,

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whilst the whole substrate was coated with uniform thickness at 300 °C. This indicates that the deposition is mass-transport-limited at the highest temperature, whereas the deposition is surface-reaction-limited at the lowest temperature. At a deposition temperature of 600 °C, the films produced from $t\mathrm{Bu}_2\mathrm{Se}$ and NbCl_5 were dark-green and powdery. They failed the Scotch tape test and the scratch test but were insoluble in the common organic solvents, they only slowly decomposed in diluted nitric acid or diluted bleach, and were stable in air for over six months. At a deposition temperature at or below 500 °C, the films had a dark-black matt appearance; they passed the Scotch tape test, but were scratched with a steel scalpel.

Due to the porous nature of the films grown from NbCl_5 and $t\mathrm{Bu}_2\mathrm{Se}$ at all the different reaction temperatures, the contact-angle measurement for water droplets was exceptionally small less than 10°. The films did not show photo-induced hydrophilic properties. This means that the surface of the niobium selenide films is unlikely to be oxide-terminated as niobium oxide shows a photo-induced reduction in the contact angle. Furthermore, this low contact-angle measurement means that water readily permeates the film and is related to high porosity.

The SEM images for the films deposited at the onset deposition temperature (300 °C) show ca. 0.2 µm plates in a perpendicular orientation to the substrate (Figure 1). The SEM images for the films deposited between 300 and 600 °C show a series of hexagonal platelets, which become longer and thicker with increasing deposition temperature. The average length of the platelets was 0.2 µm for the films deposited at 400 °C, up to 0.6 µm at 600 °C. This change in platelet size can be related to faster growth kinetics and smaller numbers of nucleation sites at the higher temperatures.

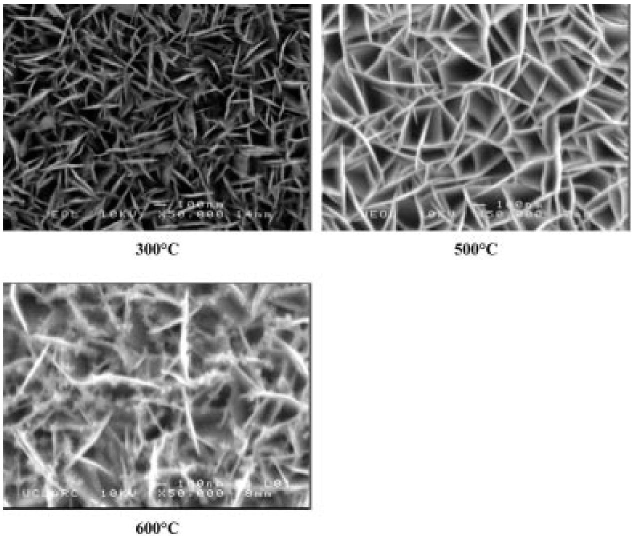
300°C
500°C
600°C

Figure 1. Scanning electron micrographs of the films produced from the APCVD of NbCl_5 and $t\mathrm{Bu}_2\mathrm{Se}$ at substrate temperatures of 300, 500 °C and 600 °C.

The films produced at a deposition temperature of 600 °C showed exactly the Nb/Se ratio expected for NbSe_2 by EDAX [$\mathrm{Nb}_{1.00(3)}\mathrm{Se}_{2.00(3)}$]. No chlorine, carbon or other contamination was found by the EDAX in these films. The films deposited at substrate temperatures below 500 °C were selenium rich with a niobium to selenium ratio of 1:2.5 at 350, 450 and 500 °C. This could indicate the co-formation of NbSe_3 or NbSe_4 or elemental selenium which would raise the selenium content. No chlorine contamination was found in the films except those produced at the very lowest deposition temperature (300 °C), and then it was at trace levels ca. 1 atom%.

An X-ray photoelectron spectrum of the niobium 3d peak for the film from di-*tert*-butyl selenide and NbCl_5 revealed the presence of two different environments in the film (Figure 2). The peaks at 203.2 eV and 205.9 eV can be respectively assigned to the Nb $3d_{5/2}$ and Nb $3d_{3/2}$ peaks of the niobium diselenide. The peaks at 207.3 eV and 210.0 eV can be assigned to the Nb $3d_{5/2}$ and Nb $3d_{3/2}$ peaks of niobium oxide $\mathrm{Nb}_2\mathrm{O}_5$. This data suggest that the uppermost surface is partially oxidised. The XPS of the selenium 3d peak for the same NbSe_2 film shows that there are also three selenium environments present (Figure 3). The peaks at 52.9 eV and 53.8 eV can be respectively assigned to the Se $3d_{5/2}$ and Se $3d_{3/2}$ peaks of the niobium diselenide. The doublet peaks at 54.1 eV, 55.0 eV and 54.6 eV, 55.5 eV can be respectively assigned to selenium and selenium dioxide. These assignments are a little tentative because a range of different curve fittings could be employed.

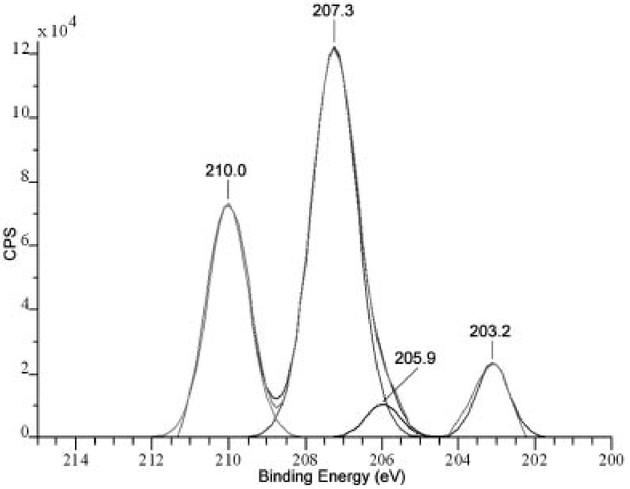

Figure 2. X-ray photoelectron spectrum of the Nb 3d peaks from the surface of a film deposited from the reaction of NbCl_5 and $t\mathrm{Bu}_2\mathrm{Se}$ at 600 °C.

Glancing-angle X-ray powder diffraction of the films showed that the reflections matched the reference spectrum for $2\mathrm{H}_a$-NbSe_2 (JCPDS File No. 018–0923) (Figure 4). The films produced at 600 °C were highly crystalline. Interestingly, measuring the XRD pattern sequentially from the leading edge of the film until the back of the film showed that the preferred orientation became significantly more pronounced with distance from the reactor inlet. The preferential orientation in the first centimeter of the coating from the reactor inlet showed some (101) texturing, al-

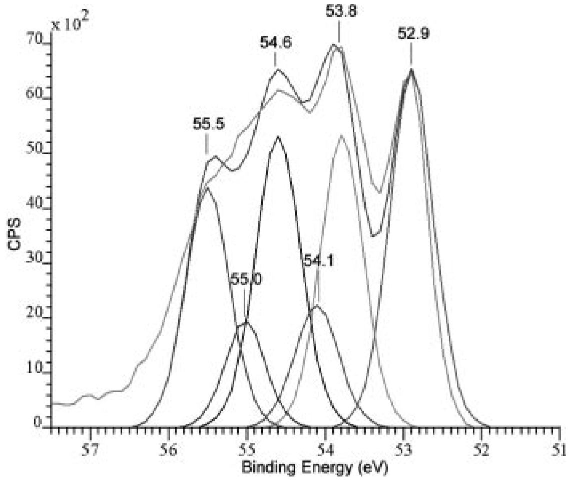

Figure 3. X-ray photoelectron spectrum of the Se 3d peaks from the surface of a film deposited from the reaction of NbCl$_5$ and *t*Bu$_2$Se at 600 °C. Outermost line is the actual data.

though the diffraction peaks were similar to the intensity stick pattern found in the literature. Very strong preferential growth along the (002) direction was shown in the next centimeter. Notably no preferential orientation was noticed in the films grown at lower substrate temperature. The indexed cell constants found for the films grown at 600 °C, a = 3.44 Å and c = 12.58 Å, compare well with the literature for hexagonal NbSe$_2$ a = 3.44 Å and c = 12.55 Å. The films grown at lower substrate temperatures all matched the literature diffraction patterns for 2H-NbSe$_2$ with the anticipated intensities and peak positions – however a detailed analysis of the cell constants indicated that they all tended to have slightly smaller a values than stoichiometric NbSe$_2$.

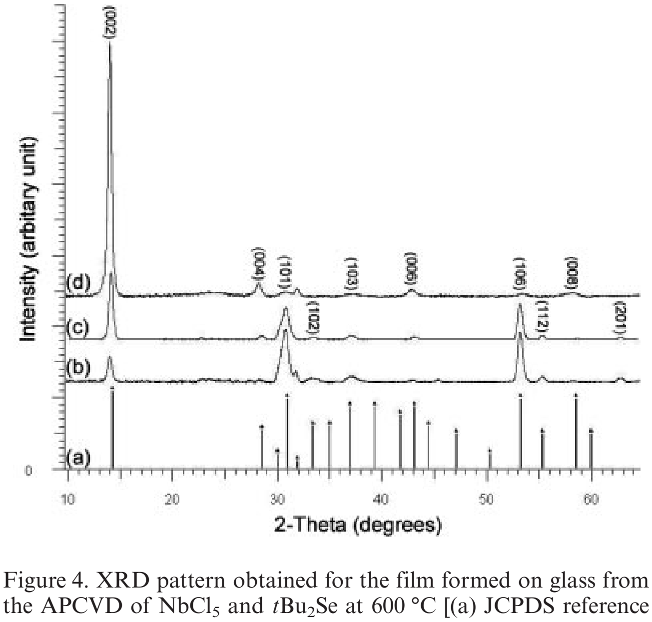

Figure 4. XRD pattern obtained for the film formed on glass from the APCVD of NbCl$_5$ and *t*Bu$_2$Se at 600 °C [(a) JCPDS reference file; (b) 0.5 cm, (c) 2 cm and (d) 4 cm from the front of the substrate].

Raman analysis of the films produced at 600 °C was identified as the distinctive 2H-NbSe$_2$ Raman pattern from the literature with a wide peak at 180 cm^{-1} and a strong peak at 228 cm^{-1} with a shoulder at 238 cm^{-1} (Figure 5).[9–12] Raman analysis of the films produced at a substrate temperature of 500 °C or below show a similar Raman pattern with two strong bands around 182 cm^{-1} and 245 cm^{-1} and a smaller peak at 310 cm^{-1} (Figure 6). This pattern is different to the one formed at higher temperature, the peaks are broader and an additional peak is seen at 309 cm^{-1}.

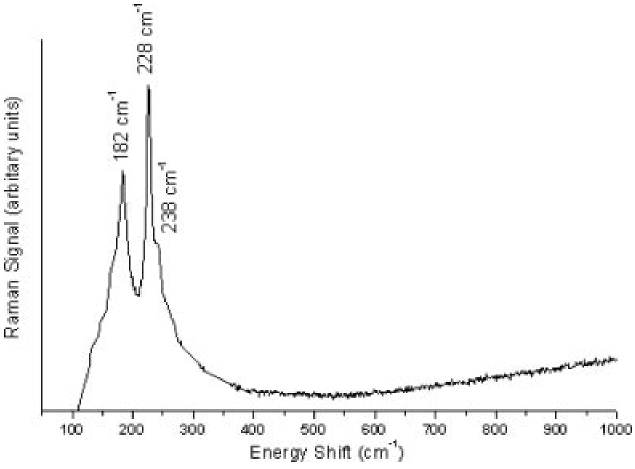

Figure 5. Raman pattern obtained for the film formed on glass from the APCVD of NbCl$_5$ and *t*Bu$_2$Se at 600 °C.

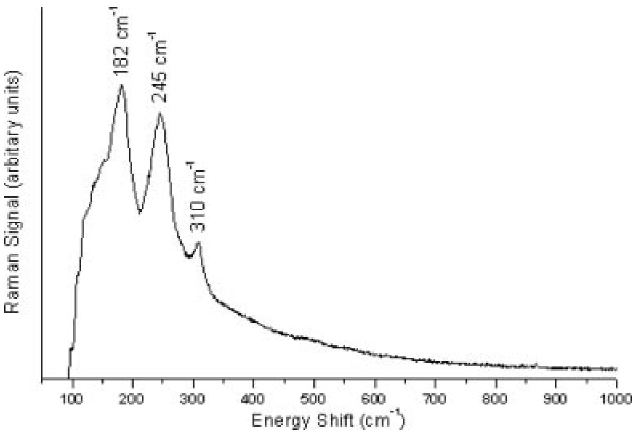

Figure 6. Raman pattern obtained for the film formed on glass from the APCVD of NbCl$_5$ and di-*tert*-butyl selenide at 300 °C.

Preferred Orientation with Pathlength

The detection of changes in preferred orientation for the NbSe$_2$ thin film grown at 600 °C with deposition position along the substrate is highly unusual for a CVD process. The substrate was made of the same glass along its length and the substrate temperature was independently checked with an external thermocouple at different points on the glass and shown to be uniform. Thus the differences in preferred orientation cannot be attributed to temperature or substrate effects. Notably, the changes in preferred orientation only occurred at the highest deposition temperature and became more noticeable with distance along the substrate. At 600 °C the deposition was only ca. 6 cm along the substrate, and the reaction had changed over from a surface-reaction-limited regime as seen at 500 °C, to a mass-transport-limited regime. Thus, along the length of the reactor the reaction becomes depleted in precursor. This depletion, therefore, has an effect on the growth of the crystallites – with growth in one particular direction being favoured under more dilute precursor conditions. Additionally, the diffusion effects of reactants and exhaust products through the boundary layer change with position along the reactor. This change over in preferred orientation is in part a consequence of the reactor design. A 'shower head' design reactor where multiple channels of reactants are used perpendicular to the substrate would be unlikely to show this effect.

A New Superstoichiometric $NbSe_{2+x}$ Phase?

We have previously studied the analogous formation of NbS_2 films from the reaction of $NbCl_5$ and tBu$_2$Se and *tert*-butylthiol.[13] In this case crystalline films were only found at substrate temperature above 500 °C, whereas the films formed in this study were crystalline at 300 °C and above. Furthermore, under some conditions EDX revealed that superstoichiometric $NbS_{2.4}$ was formed. This superstoichiometric material had similar principle Raman bands and intensity distribution (187, 242 and 298 cm^{-1}) to those formed in this study for the superstoichiometric $NbSe_2$ films.[14]

The films grown at substrate temperatures of 300–550 °C were all superstoichiometric – $NbSe_{2+x}$ (x = 0.4–0.6) by EDX analysis. X-ray powder diffraction, Raman and spot EDX analysis did not detect any free selenium metal in these films. Furthermore, none of these techniques showed the presence of higher niobium phases such as $NbSe_3$ or $NbSe_4$. No other elements were found in the films – save for a slight surface oxidation (first few nanometres). As the films grown at 300–550 °C were all exceptionally similar if not the same as the 2H-$NbSe_2$ poly-type by X-ray diffraction, with the expected intensity pattern and peak positions, it is logical to assume that the excess selenium is embedded and intercalated within the structure, especially as these are layered structures with van der Waals interactions between neighbouring sheets. These films had a slightly different unit cell size with the a and c axis slightly smaller than the literature values, the difference is right at the margin for differentiation based on the 3σ criterion. Intuitively though one would expect a large increase in the cell parameters with excess selenium incorporation. A further explanation is that an amorphous phase is present with a higher selenium content that does not show up on the XRD, Raman or XPS analysis; however, given the breadth of analysis completed, this seems unlikely. Interestingly the Raman patterns were quite revealing and supportive of a similar structure type – having a slightly different pattern to that seen for the films grown at 600 °C – which matched exactly the literature pattern for 2H-$NbSe_2$. The Raman pattern of the films made at lower substrate temperatures most closely resembled that seen for our previous CVD studies of $NbS_{2.4}$.[13,14] Hence, the lower-temperature films were consistent with the formation of the 2H-$NbSe_2$ structure with some incorporated selenium. We have not found evidence of any literature reference on this type of material being reported previously.

3. Conclusion

Niobium selenide films were deposited on glass from the APCVD reaction of $NbCl_5$ and tBu$_2$Se. Between 300 and 500 °C, the films were crystalline and selenium rich with a niobium to selenium ratio of 1:2.5 at 350, 450 and 500 °C. The films produced at a deposition temperature of 600 °C showed exactly the Nb/Se ratio expected for $NbSe_2$. No chlorine, carbon or other contamination was found by the EDAX in these films. The films produced at 600 °C were highly crystalline with a preferential growth either along (101) or the (002) direction. The preferred orientation effects were more marked with distance from the reactor inlet and suggest that depletion in reagents leads to a slightly altered growth mechanism. The $NbSe_2$ films were stable in air, insoluble in the common organic solvents, and were only slowly decomposed in nitric acid. The films grown at 300–550 °C best fit the 2H$_a$-$NbSe_2$ structural type with some excess intercalated selenium.

4. Experimental Section

Caution: It should be noted that the CVD of $NbSe_2$ could produce H_2Se, which is highly toxic and malodorous. All the experiments should be conducted in a fume cupboard and the gas from the CVD process treated with bleach (with an associated copper sulfate indicator bubbler, to check the bleach is working) to destroy the possible presence of H_2Se. After the CVD synthesis the $NbSe_2$ films were treated as air sensitive although subsequent analysis showed that they were indefinitely air stable.

Chemical Vapour Deposition Studies: Depositions experiments were carried out under dinitrogen (99.99%) on glass substrates using a horizontal-bed cold-wall APCVD reactor. The glass substrate was a SiO_2-precoated (ca. 50 nm thick SiO_2 barrier layer) standard float glass (Pilkington, UK) 15 cm × 4 cm × 0.3 cm. The substrate was heated by a graphite block and the nitrogen carrier gas was preheated to 110 °C by being passed along 2 m lengths of coiled stainless-steel tubing inside a tube furnace.

Niobium pentachloride was obtained from Aldrich Chemical Co. and di-*tert*-butyl selenide was supplied by Epichem. They were both used without further purification. The di-*tert*-butyl selenide and $NbCl_5$ were placed into two different stainless-steel bubblers, which were both heated by a jacket. They were both introduced into the gas streams by passing hot N_2 through the bubblers. The bubbler temperatures and flow rates were kept constant to 90 °C and 0.5 L·min^{-1} (67.4 mmol·min^{-1}) for the tBu$_2$Se bubbler and to 210 °C and 2.0 L· min^{-1} (47.8 mmol·min^{-1}) for the niobium pentachloride bubbler (Table 1). The flow rate through the mixing chamber was between 1.9 and 4.6 L·min^{-1} for all depositions.

Table 1. EDAX, Raman and X-ray diffraction data for the films produced by APCVD reaction of $t\mathrm{Bu}_2\mathrm{Se}$ with $NbCl_5$.

Deposition temperature	XRD (lattice constant in Å+/– 0.01 Å)	Raman	EDAX
250 °C	–	–	No film
300 °C	2H-$NbSe_2$; a = 3.36, c = 12.47	182 + 245 + 310	$NbSe_{2.4}$
350 °C	2H-$NbSe_2$; a = 3.37, c = 12.59	183 + 248 + 309	$NbSe_{2.5}$
400 °C	2H-$NbSe_2$; a = 3.42, c = 12.56	184 + 248 + 310	$NbSe_{2.6}$
450 °C	2H-$NbSe_2$; a = 3.36, c = 12.63	183 + 247 + 309	$NbSe_{2.5}$
500 °C	2H-$NbSe_2$; a = 3.41, c = 12.63	183 + 246 + 309	$NbSe_{2.5}$
600 °C	2H-$NbSe_2$; a = 3.44, c = 12.58	2H-$NbSe_2$	$NbSe_2$

The reaction of $t\mathrm{Bu}_2\mathrm{Se}$ and $NbCl_5$ was studied in the temperature range from 250–600 °C. The deposition time for all experiments was 1 min. At the end of the deposition, the bubbler line was closed and the substrate was cooled under nitrogen in the reactor. Then the substrates were handled briefly in air before storage under dry, oxygen-free nitrogen in a glove box. Analyses were performed for each sample on a 2 cm × 4 cm band cut 2 cm from the front of the substrate.

Film Analysis: X-ray diffraction patterns were measured with a Bruker X-pert diffractometer using monochromated Cu-$K_{\alpha 1}$ radiation ($K_{\alpha 1}$ = 1.5406 Å). The system had a focus and movable x-y stage to analyse various portions of the film. The diffractometer used glancing incident radiation (1.5°). The samples were indexed using unit cell and compared to database standards. EDAX was obtained with a Philips XL30ESEM instrument and SEM was obtained with a JEOL 6301 instrument. UV/Vis-NIR spectra were recorded in the range 190–1100 nm using a Helios double-beam instrument. Reflectance and transmission spectra were recorded between 300 and 1200 nm with a Zeiss miniature spectrometer. Reflectance measurements were standardised relative to a rhodium mirror and transmission relative to air. Raman spectra were acquired with a Renishaw Raman System 1000 using a helium-neon laser of wavelength 632.8 nm. The Raman system was calibrated against the emission lines of neon. X-ray photoelectron spectroscopy was undertaken with a VG ESCALAB 220I XL instrument with focussed (300 µm spot) monochromatic Al-K_α radiation at a pass energy of 20 eV. Scans were acquired with steps of 50 meV. A flood gun was used to control charging. Binding energies were referenced to an adventitious C 1s peak at 284.6 eV (this peak is due to residual pump oil used in the XPS high vacuum system- but is removed on the first argon ion etching). Argon sputtering was used for approximately 1 minute in a rastering mode in order to remove surface contamination.

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