

Supplementary Information

to the article:

Face-centred cubic carbon as a fourth basic carbon allotrope with properties of intrinsic semiconductors and ultra-wide bandgap

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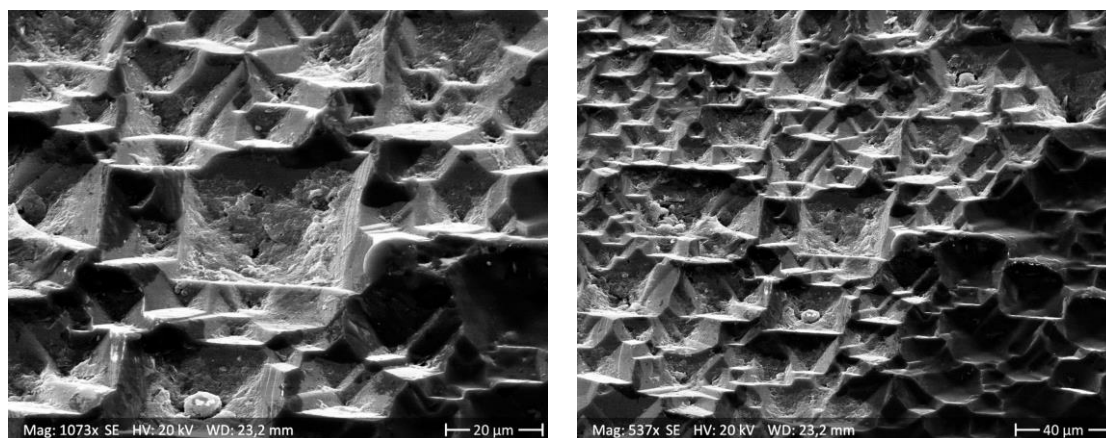


Figure S1. HRSEM images of the as-deposited sample surface obtained at an angle of view 30°.

The positions of the (200)-, (220)-, (222)- and (400) reflexes obtained by XRD in Table 1 correspond to the same obtained by electron diffraction and agree reasonably well with the crystal lattice constant reported in literature¹ ($a_0=3.563$ Å). However, the d_{111} -value obtained by XRD noticeably differs from the one determined from electron diffraction and from the one reported in literature. This difference can be explained by the nonuniform distortion of the cubic crystal lattice reported in ref.².

To better understand this issue, we undertook additional studies. An appearance of the forbidden diffraction maxima such as (200)- and (222)-ones in diamonds was originally recognized by M. Renninger as a “detour excitation”³. Still in the classical work of K. Lonsdale *et al.*⁴ the system of diffraction maxima corresponding to the carbon face-centred cubic phase was found from tiny particles present in a mixture with synthetic diamonds. In fact, scientists have been reporting over decades the electron diffraction patterns corresponding to this phase in form of nanoparticles (see **Introduction**). However, no XRD pattern was obtained from single-crystalline *fcc*-carbon samples (epitaxial films or bulk crystals) so far. Main reason for that to name were: (i) challenging (time consuming) synthesis of this material in large enough amounts and (ii) significantly weaker interaction between carbon atoms and X-rays in contrast to that for electron beams⁵.

M. Renninger explained an occurrence of the (200) and (222)-reflexes forbidden for the diamond crystal lattice by a detour excitation yet in 1937³. The attributes of this phenomenon were poor reproducibility of reflectivity for forbidden reflections and inexplicable multitenfold increase of those diffraction maxima at certain conditions. Our XRD measurements revealed some deviations of both (200)- and (222)-diffraction maxima, which are forbidden for the diamond crystal lattice, when examining different areas of the sample surface, however, these deviations were only up to about 30% of the maximum intensity (the corresponding X,Y-scans are not shown here). Considering the extremely rough surface of the sample (see Fig. S1), which is likely to cause some deviation in the maxima intensity, one can exclude the detour excitation in our case.

We also draw attention to the ratio between intensities of the diffraction maxima from the diamond substrate and the film, which is close to nearly two orders of magnitude. There is no broadening of maxima at large 2 Theta angles apparently indicating the absence of residual stresses in the film. Nevertheless, as it was established at scratching of the *fcc*-carbon film by a diamond needle, this material appeared to be extremely soft and ductile. So, its significant lattice distortions can presumably occur at negligibly low residual stresses.

There are however two issues which require special consideration: (i) splitting the (200)-reflex, which is inconsistent with the shape of the (400)-one, and (ii) variation of the lattice constant calculated on the basis of different diffraction maxima, in particular, on the basis of the (111) reflection ($\sim 3.596 \text{ \AA}$) and on the basis of the other four reflections (nearly $3.556\text{--}3.563 \text{ \AA}$). To avoid a systematic failure in this case, we proved that the lattice constant of the diamond substrate does not change with $\sin^2\psi$, where the set ψ value was varied from 0° to 55° .

In this respect one should consider surface morphology of the sample in more detail (Fig. S2). As one can see, the surface is dotted with square craters obtained as a result of etching the diamond substrate in the hydrogen plasma. It is important to point out that the square craters are twisted by 45° to the substrate side, which was confirmed by the images obtained by optical microscopy (Fig. S3a). This disposition points are located symmetrically as a result of the formation of the (111)-facets, which are known to predominantly form on polycrystalline diamond nuclei at relatively low deposition temperatures ($< 900^\circ\text{C}$)⁶. One can also see that some craters are filled with a substance that looks dark on the SEM images (Fig. S2). The appearance and examination results of FIB lamellae prepared from the coated diamond substrate and examined by transmission electron microscopy (not shown here) indicate that the dark substance consists of *fcc*-carbon; the thickness of the film in the regions corresponding to the craters' bottoms is in the μm -range. The *fcc*-carbon film is significantly thinner in the areas located on the slopes of the craters (by up to one order of magnitude).

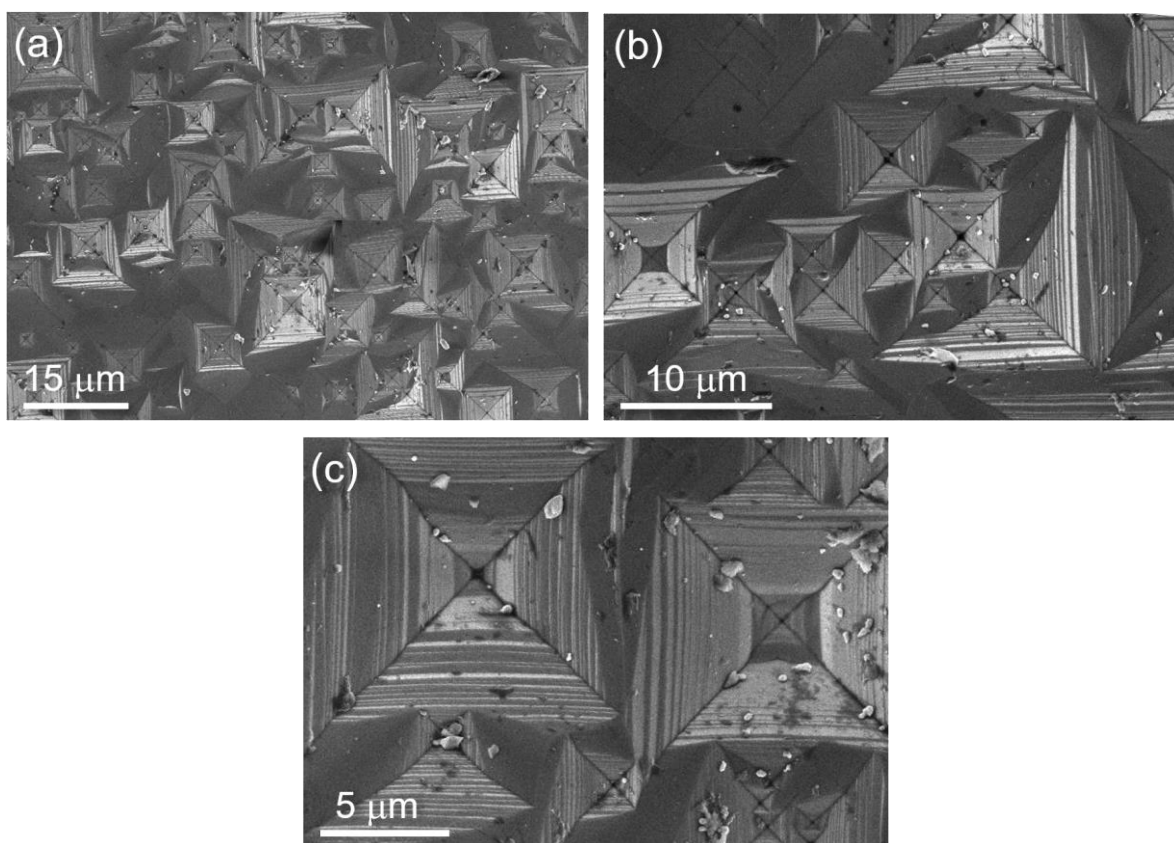


Figure S2. Plane-view SEM images of the *fcc*-film. The surface morphology results from the etching of the (100)-diamond substrate surface in a hydrogen plasma followed by deposition of the *fcc*-carbon film. Images (a), (b) and (c) were taken for auspicious places at different magnifications.

Since the SEM images clearly show stepped slopes on the craters' surfaces, a more detailed investigation of those craters was undertaken (Fig. S3). Particularly, AFM measurements were performed to establish the curvature angle. The linear profiles obtained in different directions across the AFM maps gave different curvature angles of the hollows varying within the range of $\sim 127^\circ - 143^\circ$ (Fig. S3b). This is inconsistent with the expected angle between the (111)-facets, which is expected to vary in the range of nearly $70^\circ - 90^\circ$. This fact explains the appearance of the steps and indicates that they are formed by the (100)- and (110)-facets which are the horizontal and vertical sides respectively. Fig. S3c shows how the footprint of each θ - 2θ measurement plane correlates with the position of the crater. The scheme shown in

Fig. 3d demonstrates how the path of X-rays diffracting on the certain crystallographic planes relates to the surface of the crater in the case when the sample was not tilted ($\psi \approx 0^\circ$). Presumably, in this case it is a matter of very peculiar diffraction conditions. In case of the (200)-diffraction the incident beam has grazing angle of $\theta \approx 0.6^\circ$ respective to the craters' slope. Hence it can give an intensive signal for the thinner film regions located in the craters' slope area, whereas the dark faceted plane could prominently be shadowed. The facets are tilted with respect to the beam plane at an angle of $\sim 25^\circ$ and can give only a weak (200)-diffraction maximum. The bottom regions where the film is significantly thicker should provide a noticeably stronger (200)-peak. Thus, if *fcc*-carbon has a lattice constant other than that of diamond, significant nonuniform crystal lattice distortions can form on the facets and edges of the films' craters presumably comprising large areas of twinning. Also, for the vertical and horizontal steps of the craters one can get different lattice spacing values. Based on considering the surface geometry, obtaining the reasonably strong (400)-diffraction peak requires more material and this diffraction peak is presumably originated solely from the thicker film regions on the bottom of the craters. This fraction of the film is however very inhomogeneous having different thicknesses in various regions.

In the case of other diffraction reflexes, tilting the sample emerges as an additional parameter. At $\psi \approx 45^\circ$ one can expect the (220)-reflex from the (100)-sides of the steps located in the craters, which are identical for any facet of the crater. Since the upper surfaces (white and grey regions shown in Fig. S3c) are basically shadowed and the incident angle exceeds 7° for the lower grey surface, it can be expected that the same thickness issue as described above takes place and a relatively weak diffraction signal is originated from this part of the film. The strongest signal should be obtained from the regions of the craters' bottoms, where the film thickness is quite high. In the case of the (111)-diffraction when the sample is tilted at $\psi \approx 55^\circ$, the two grey surfaces shown in Fig. S3c are only partially exposed to the X-ray beam. For the upper grey plane, a kind of in-plane measurement is conducted, when the angle between the sample surface and the θ - 2θ plane is equal to $\sim 8^\circ$. In this case the diffraction signal from only the (100)-facets can be detected, whereas the diffraction signals can be detected from both facets of the steps located on the low grey surface shown in Fig. S3c. This stipulates the appreciable broadening of the XRD peaks. The (222)-diffraction maximum is obtained from the thickest film regions, which are accessible at this 2θ angle. Our suggestion in this regard is supported by a very similar intensity of two diffraction maxima that cannot be the case if they would have been recorded from the same film fractions.

These arguments also explain why no adequate trend in the $a = f(\sin^2\psi)$ dependence was established and why the interplanar distances obtained from different diffraction maxima do not give a consistent value of lattice constant for the *fcc*-carbon film.

Within technically available spectral ranges, the FTIR reflection spectrum shown in Fig. S6 does not comprise maxima that can be attributed to the known carbon-carbon bonds. The FTIR spectra shown in Fig. S6 allowed stating that the chemical bond in the carbon film has different nature than that in diamond, since no diamond specific or C-C features appeared in former case. There are also no C=C features characteristic for nanocrystalline or amorphous hydrogen containing carbon films. An overall lower reflectivity of the film as compared to diamond is caused by its higher roughness.

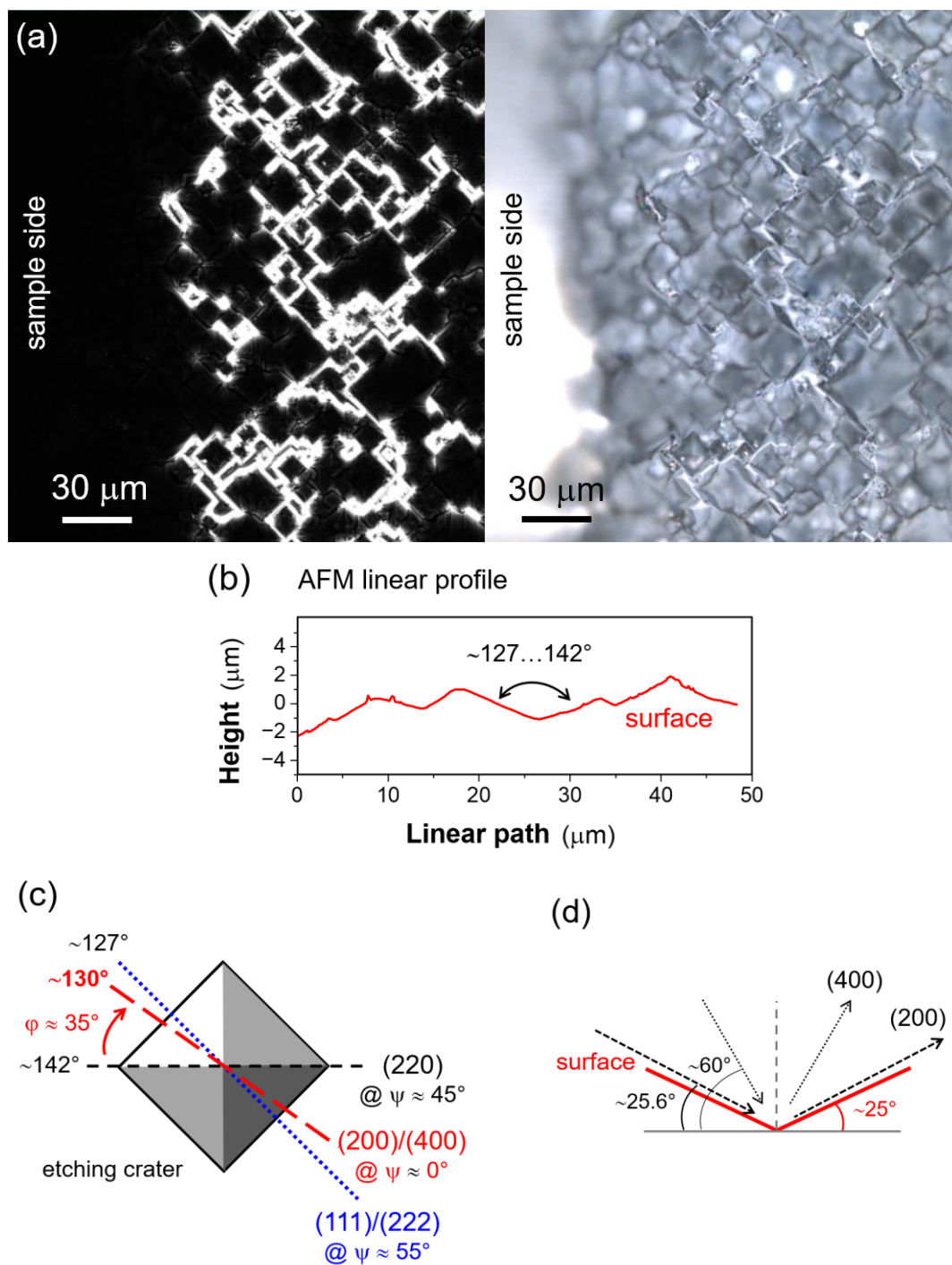


Figure S3. XRD geometry in respect to the surface morphology. (a) Plane view optical images in different acquisition modes showing the disposition of craters. (b) A typical linear AFM surface profile (about thirty profiles were analysed). (c) Sample twisting at various XRD measurements in relation to the craters (the highest I_{200} intensity was reached when the sample was twisted around φ -axis at an angle of about 35°). (d) Schematic diagram indicating the interrelation between the curvature angle of the crater and 2θ diffraction angles (to simplify, only approximate angle values are given).

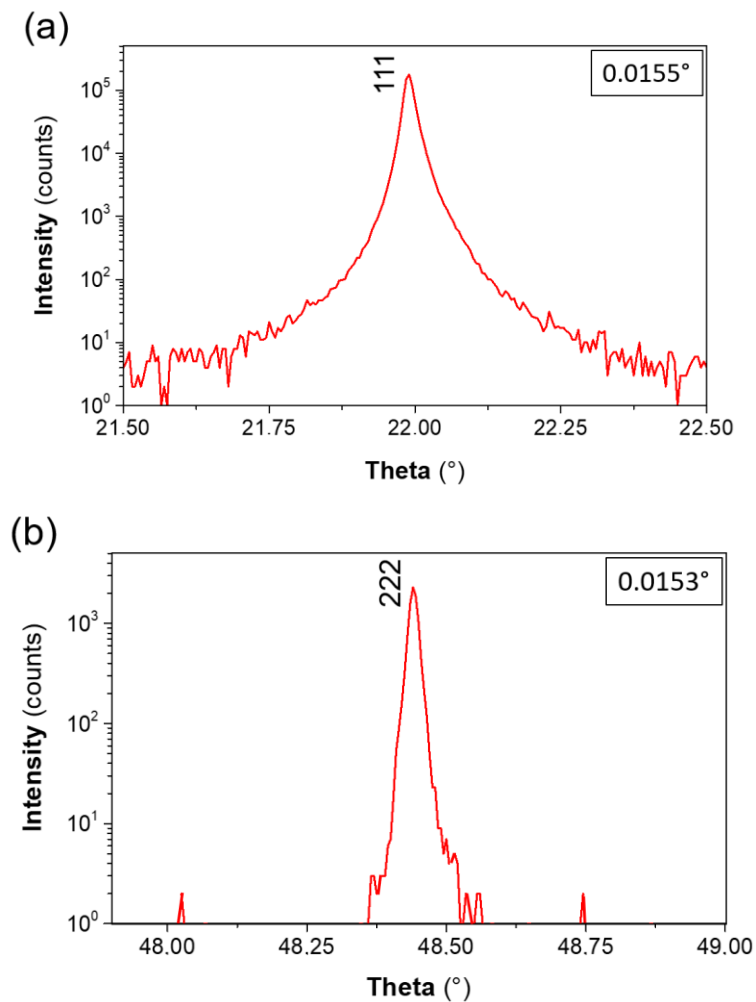


Figure. S4. Rocking curves for the interrelated reflexes of the film and the substrate. (111)-reflex of diamond (a) and the (222)-reflex of *fcc*-carbon (b) measured at the same positioning of the sample. Fitting with Lorentzian gives the FWHM values given in insets.

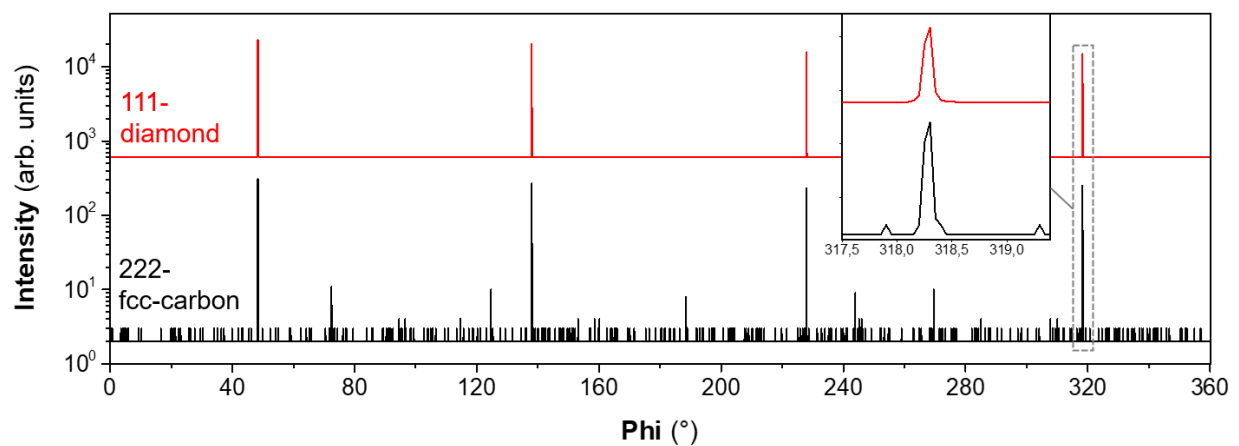


Figure. S5. Phi-scans for (111)-diamond and (222)-*fcc* cubic carbon reflexes measured at the same positioning of the sample.

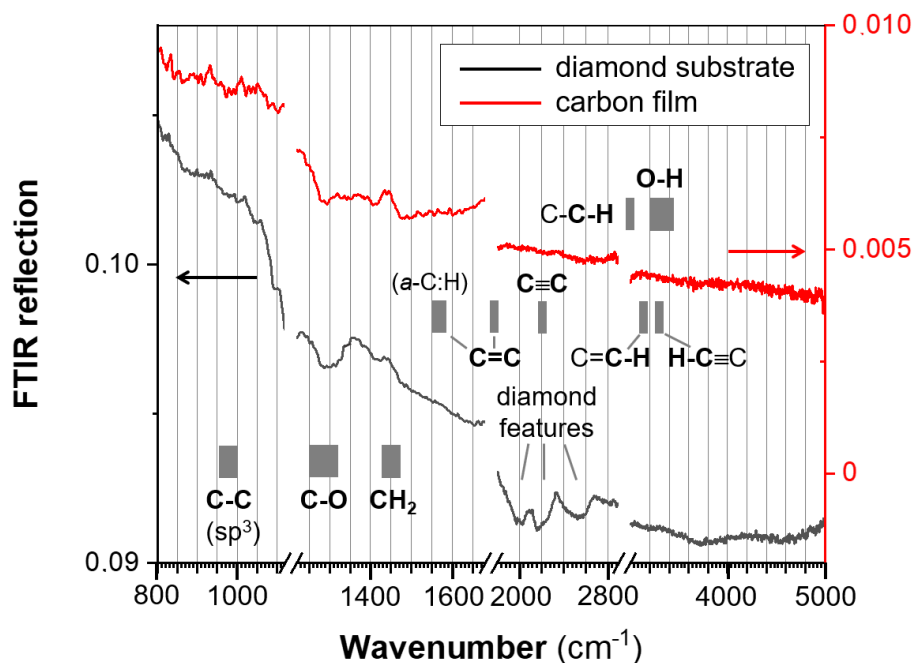


Figure S6. FTIR spectra of diamond substrate and carbon film. The breaking ranges correspond to the features dominating from the sticking holder. The characteristic vibrational modes are taken from the database⁷.

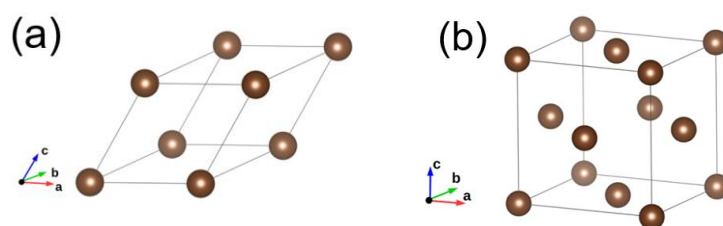


Figure S7. A comparison of different unit cells for the *fcc*-structure. (a) Primitive and (b) conventional one.

Supplementary References

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