

Supporting information

Selenium and Benzeneselenol interaction with Cu(111)

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1. Selenium on Cu(111) and Se and S coadsorption

Overview XPS spectra for the clean Cu(111) surface, after immersing into the Na₂Se solution and after heating, are shown in fig.S1a. The clean Cu spectrum shows an intense Cu 2p doublet with the Cu 2p_{3/2} core level at 932.45eV. The binding energy of the Cu 2p core level structure is calibrated against the Cu 3p taken in the same spectrum (with a small scan step), whereas the Cu 3p binding energy was calibrated to Au 4f at 84eV taken at a 260 eV photon energy.

After incubation in the Na₂Se solution, we note that there appears a peak related to O1s at around 531.2eV. We do not observe the XPS Na 2p core level peak at about 30eV and Na 2s core level structure at about 64eV, which means the Na was removed completely after rinsing. One can clearly observe the Se 3p peak at high incident photon energy.

After heating the samples to about 300°C, the intensity of the O 1s peak decreases and the Se 3d peak with binding energy at about 54eV shows up clearly. The spectra were acquired after the sample cooled down. The Se3d spectrum is seen better in the overview spectra taken with a 260eV photon energy (fig S1b) because of a higher photoionization cross section. It is observed clearly upon initial selenization. After annealing the samples to 300°C, it becomes more intense, possibly because of removal of excess Se (see main text) and contaminants. Further changes in these spectra are observed when heating to 500°C as will be described below.

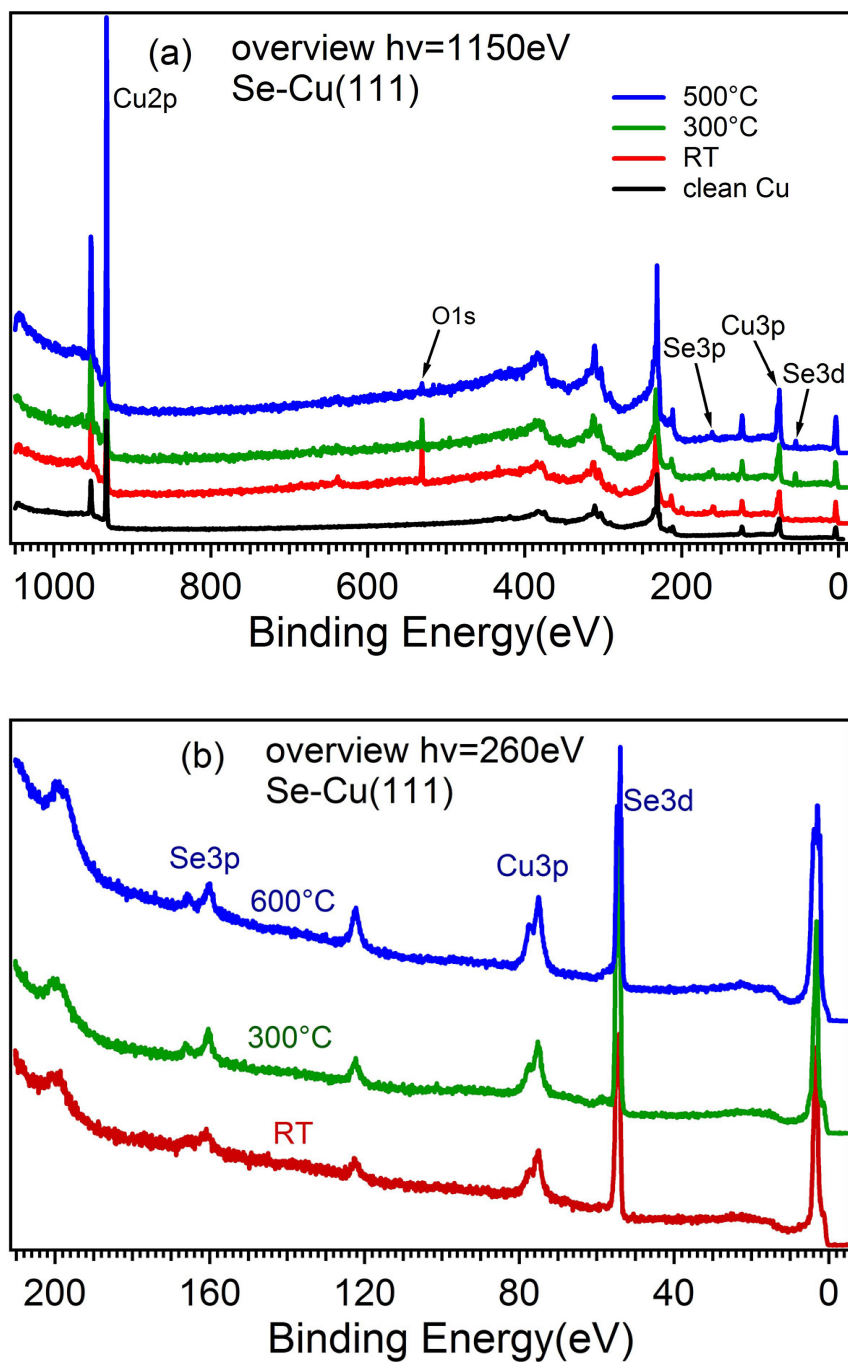


Figure S1. XPS overview spectra for Se adsorption on Cu(111) for (a) 1150 eV and (b) 260 eV photon energies. Clean surface (black line), initial Se adsorption (red line), after heating to 300 °C (green line) and after heating to 500 °C (blue line).

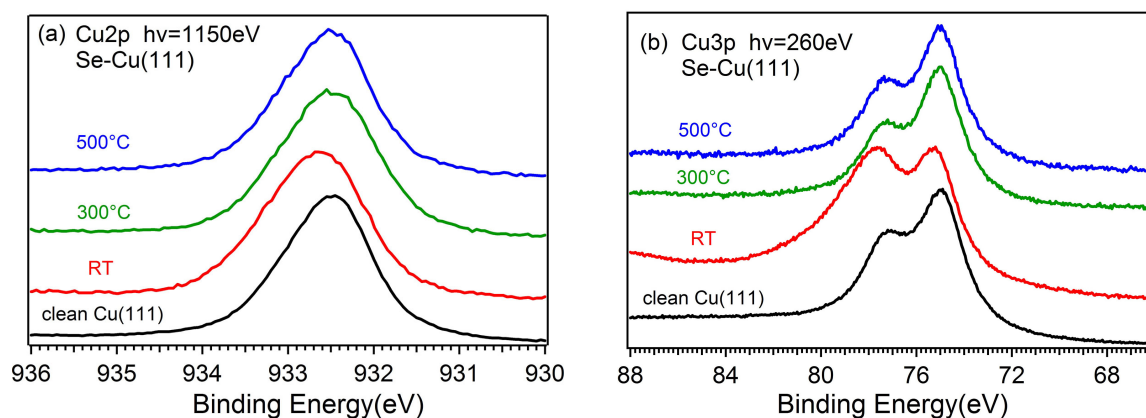


Figure.S2 XPS spectra of Cu $2p_{3/2}$ and Cu $3p$ core level after initial selenization and annealing to the indicated temperatures.

Upon initial Se adsorption in solution, the Cu $2p_{3/2}$ core level peak, which is at 932.45 eV for the clean surface, is found to shift to higher binding energy (fig.S2a). The binding energy shift towards high energy indicates strong Cu selenization (possibly accompanied by some oxidation, since we find some O after immersing into the Na_2Se solution). After annealing, the Cu $2p_{3/2}$ core level peak shifted to lower energy 932.5, which is still slightly higher than that of clean surface before selenization. The spectrum of the selenized sample also becomes broader than that for clean copper, being a superposition of signals from clean and selenized Cu.

The Cu $3p$ region taken at a 260 eV photon energy, is shown in fig.S2b. After initial selenization the Cu $3p$ structure shows a very broad peak extending to higher energies, which is presumably due to the contribution of a shake up satellite. After annealing to 300°C, this broadening disappears. The CLBE of Cu $3p_{3/2}$ peak for clean Cu(111) and after heating to 300°C and 500°C is located at about 75 eV.

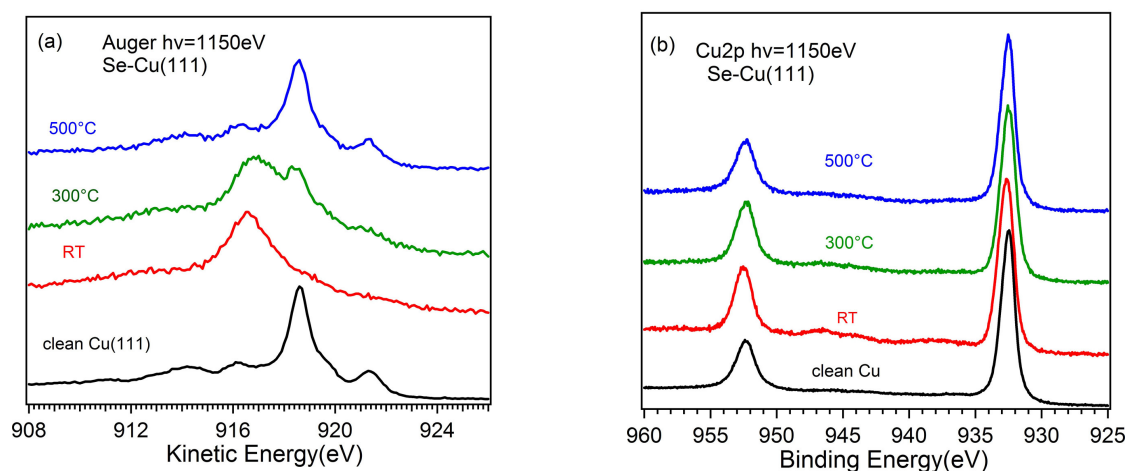


Figure.S3 Auger and Cu $2p$ XPS spectra under different temperature conditions.

The Cu LMM Auger peak for Cu(111) (fig. S3a) shows an initial displacement from the clean Cu position at 918.6eV. It has a strong component at 916.6 eV as a result of sselenization, compatible with Cu(I) and Cu(II) presence^{49,52}. After heating to 500°C the Auger spectra resemble the one for a clean surface. As shown in fig.S3b no significant satellite features were observed in the 940eV range indicating that we are dealing mainly with Cu(I) species.

In order to extract the copper selenide (Cu_{Se}) contribution, we fitted the $\text{Cu}2p_{3/2}$ peak for initial selenization and after annealing treatment, using two components corresponding to bulk Cu and relating to Cu selenide. It should be emphasized that we refer here to the “surface selenide” contribution Cu_{Se} for both strong selenization and the Se phases that appear after annealing. For bulk Cu we took the clean Cu line profile, with a peak at 932.45eV. As shown in fig. S4a, we then get the Cu_{Se} peak contribution. The Cu_{Se} peak decreases in magnitude, when going from initial selenization to the annealed samples and its energy shifts from 932.75 to 932.95V.

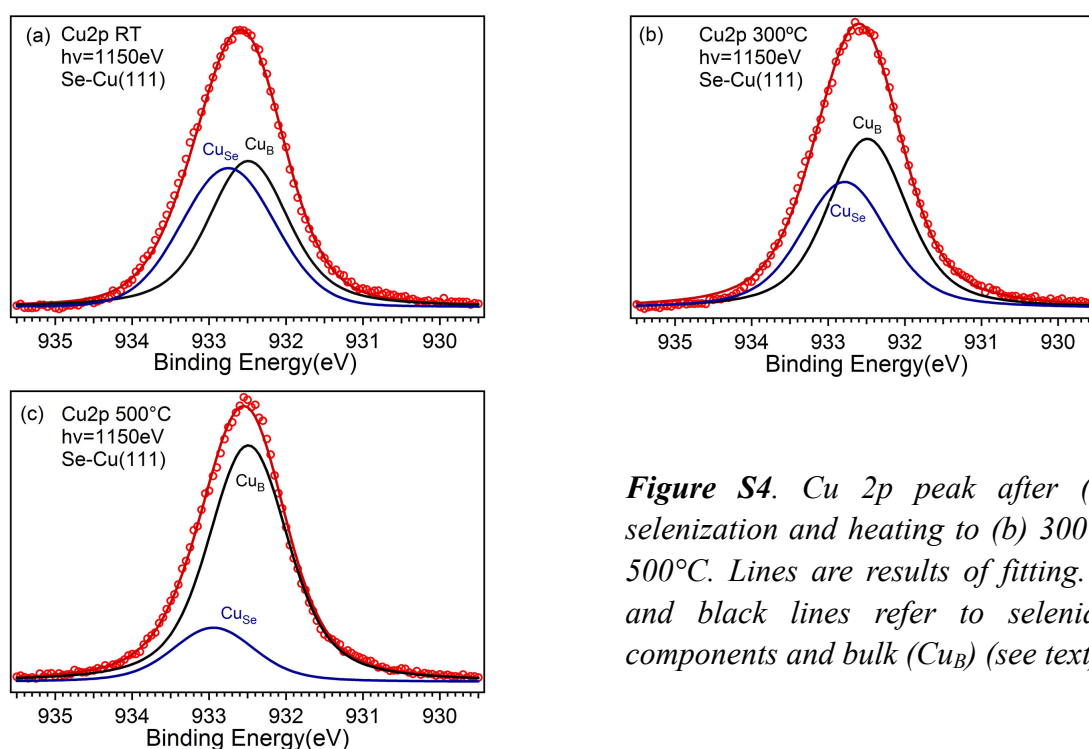


Figure S4. Cu 2p peak after (a) initial selenization and heating to (b) 300°C and (c) 500°C. Lines are results of fitting. The blue and black lines refer to selenide (Cu_{Se}) components and bulk (Cu_{B}) (see text).

All these data indicate that a decrease of Se concentration occurs with heating. Note that the melting temperature of bulk Se is about 220°C, while its boiling temperature is 685°C so that any bulk like Se multilayer may be expected to have been removed. LEED images for clean Cu and after selenization and annealing are shown in fig.S6. These indicate the appearance of complex submonolayer ordered chemisorbed Se structures.

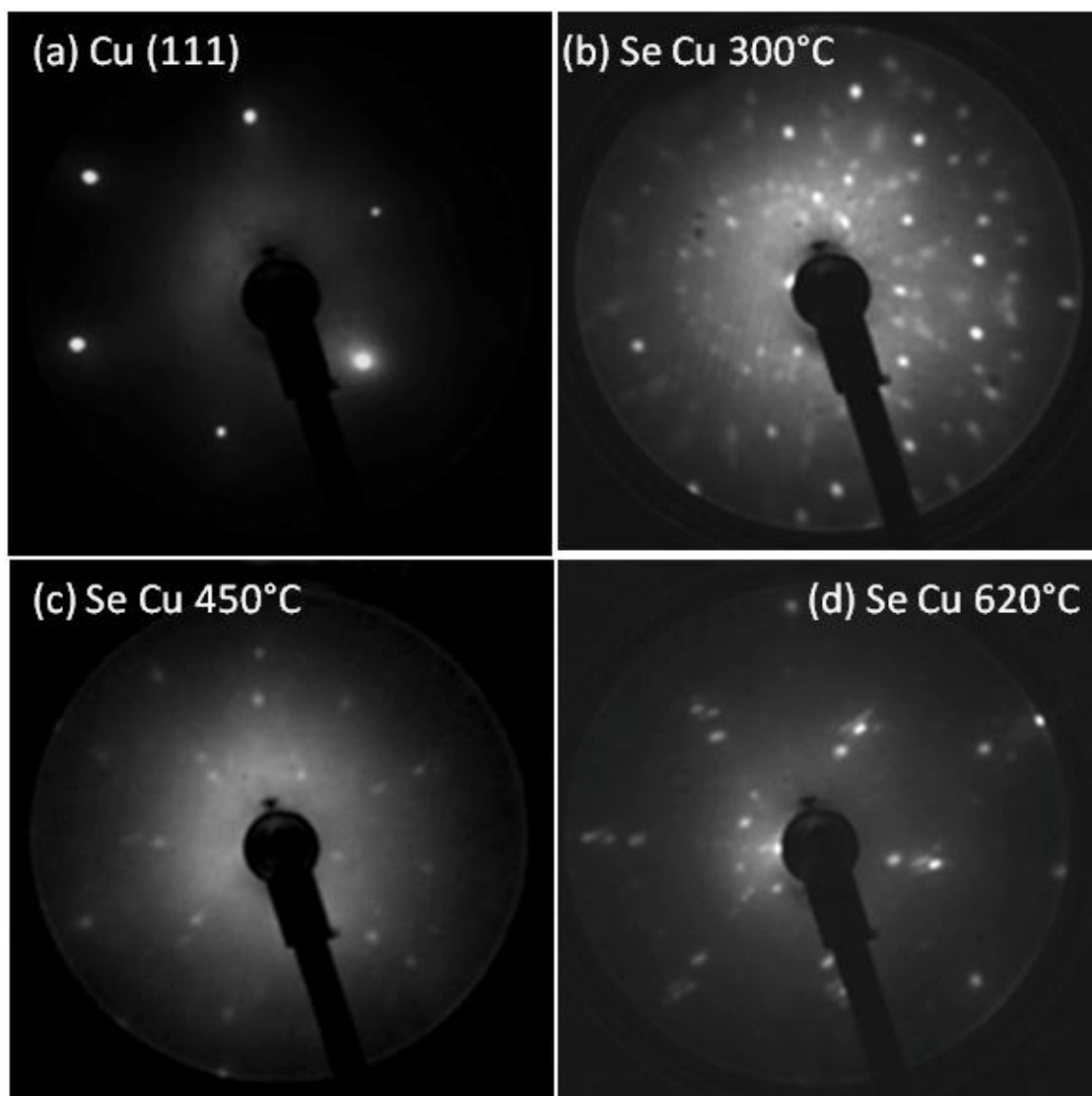


Figure S5 LEED image for Se adsorption on Cu(111) after heating by 500°C. (a) 150 eV, (b) 50 eV, (c) 83 eV, (d) 60 eV

Coadsorption of Se and S

Overview XPS spectra for two photon energies for Se and S coadsorption from equal proportion Na_2S and Na_2Se solution are shown in fig. S6 upon initial adsorption and after heating. One can observe the stronger intensity of the S2p peak after heating to 300°C and the progressively increasing intensity of the Se3d peak.

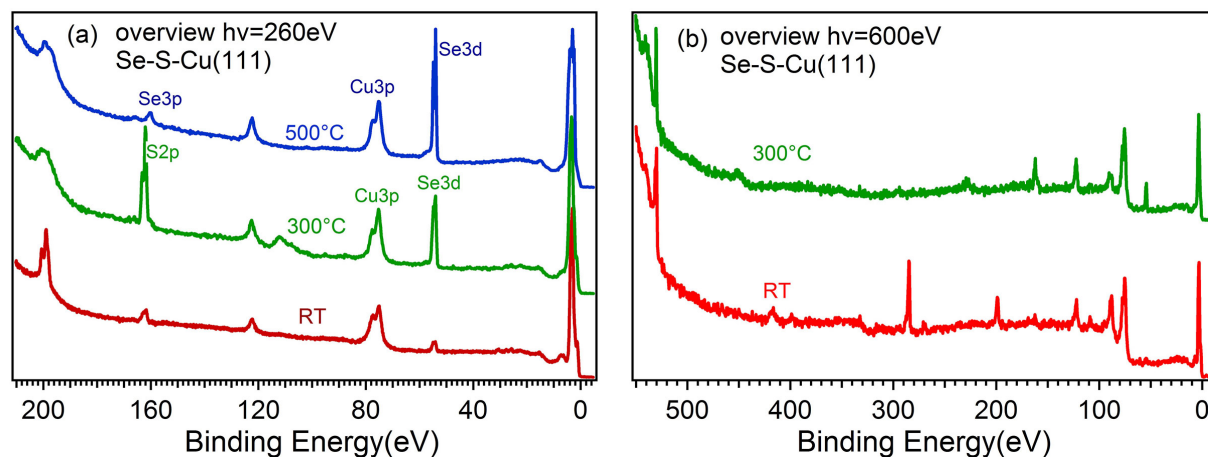


Figure S6 Overview XPS spectra for two photon energies for Se and S coadsorption on Cu(111).

XPS spectra in the Cu3p and Se 3p/S2p regions are shown in fig S7. As for the case of only Se adsorption, after initial selenization the Cu 3p peak is broad presumably due to the contribution of a shake up satellite. After annealing this broadening disappears. The CLBE of Cu 3p_{3/2} peak after annealing is located at about 75eV.

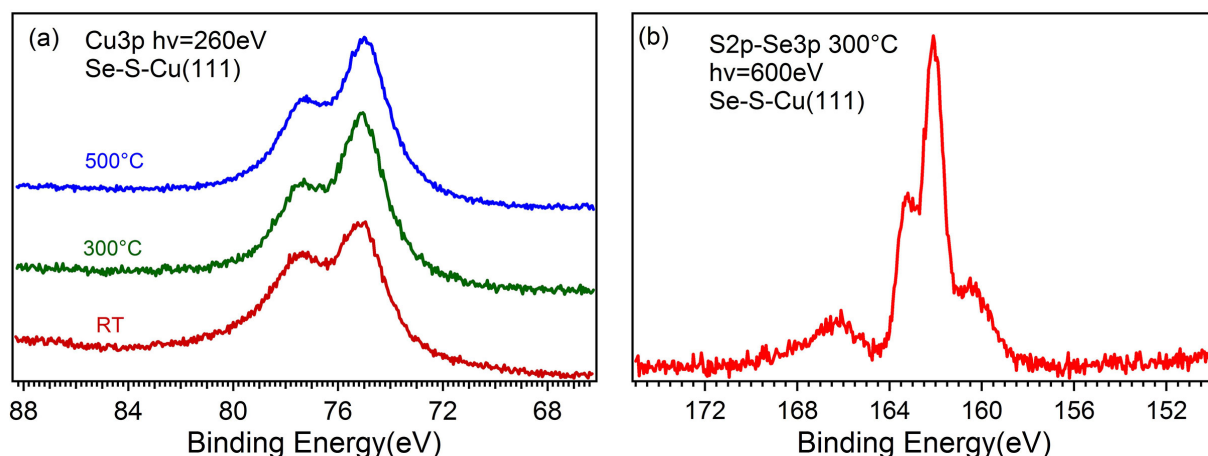


Figure S7. XPS spectra in the Cu3p and Se 3p/S2p regions.

The XPS spectrum in the S2p/Se3p region (fig S7b) was taken at 600eV energy since here the photoionisation cross sections are the same for both states. As opposed to the case of the 260eV photon energy spectrum shown in fig.4a., here the Se contribution is much more apparent as mentioned in the main text. The shape of the Se3p_{3/2} peak was fitted using the profile of the Se3p_{1/2} component and the areas of the S and Se peaks thus extracted turn out to be the same to within 10%. This would indicate that the two are present in almost equal proportions. However for an accurate determination one needs to know the structure of the layer in order to estimate attenuation effects in electron scattering, which we lack.

LEED images after Se and S coadsorption and annealing are shown in fig.S7

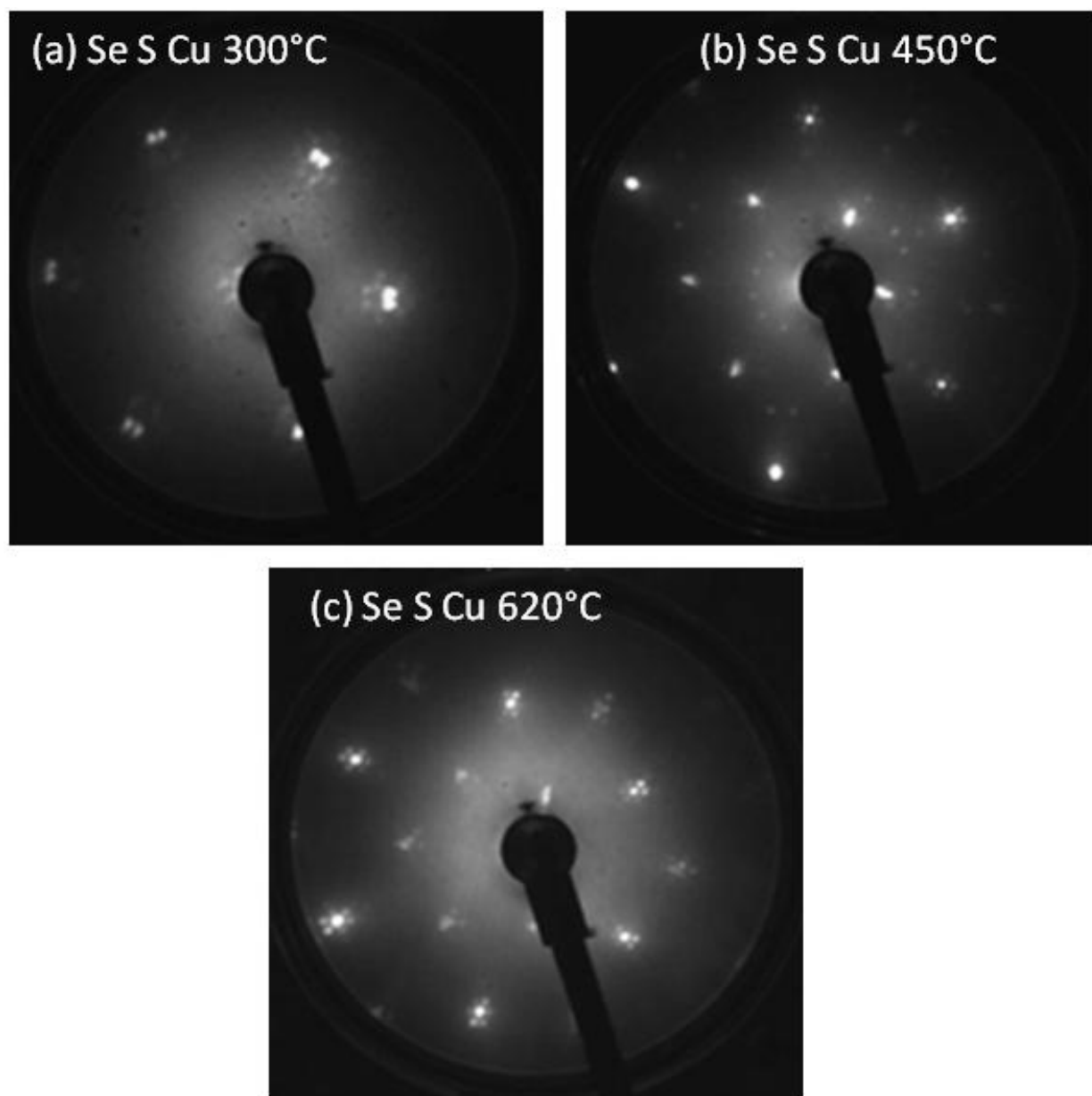


Figure S8. LEED images after Se and S coadsorption and annealing to the indicated temperatures. Electron energy (a)55eV (b) 120eV (c)150eV.

2. BSe adsorption on Cu XPS spectra: damage control.

In order to study effects of X ray beam damage on the shape of the XPS spectra and in particular check if the A peak, which we attribute to atomic Se (see main text) is not induced by irradiation, we acquired spectra scan by scan. The figures below show the comparison of the first and last (6th) scans for the Se 3d peak (fig.9Sa) and a colour map of the intensities (fig.9Sb). These data do not reveal any changes in the spectra and thus there is no obvious beam damage detected here. It should be noted that this does not preclude C-C bond cross linking in the layer as this is known to occur for aromatic thiol SAMs.^{S1}

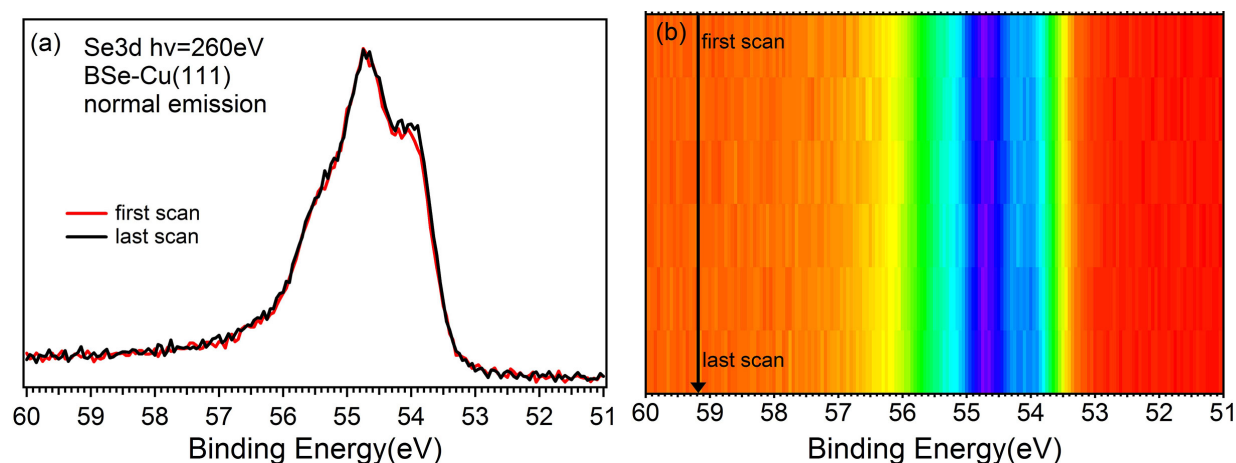


Figure S9. (a) The first and last (6th) scans for the XPS Se 3d peak and (b) a colour map of the intensities in the spectrum from the first to last scan.

References.

S1. A. Turchanin and A. Götzhäuser, *Progress in Surface Science*, 2012, **87**, 108–162.