Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Preferential S/Se occupation in anisotropic $ReS_{2(1-x)}Se_{2x}$ monolayer alloy

Wen Wen,[a, e] JunhaoLin,[b] KazuSuenaga,[b] YuzhengGuo,*[c] YimingZhu,[a]

Hung-Pin Hsu,[d] and Liming Xie*[a, e]

[a]CAS Key Laboratory of Standardization and Measurement for Nanotechnology, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, P. R. China.

E-mail: xielm@nanoctr.cn

[b]National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8565, Japan

E-mail: suenaga-kazu@aist.go.jp

[c]College of Engineering, Swansea University, Swansea, SA1 8EN, United Kingdom

E-mail: yuzheng.guo@swansea.ac.uk

[d]Department of Electronic Engineering, Ming Chi University of Technology, Taipei 243, Taiwan, Republic of China

[e]University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China.

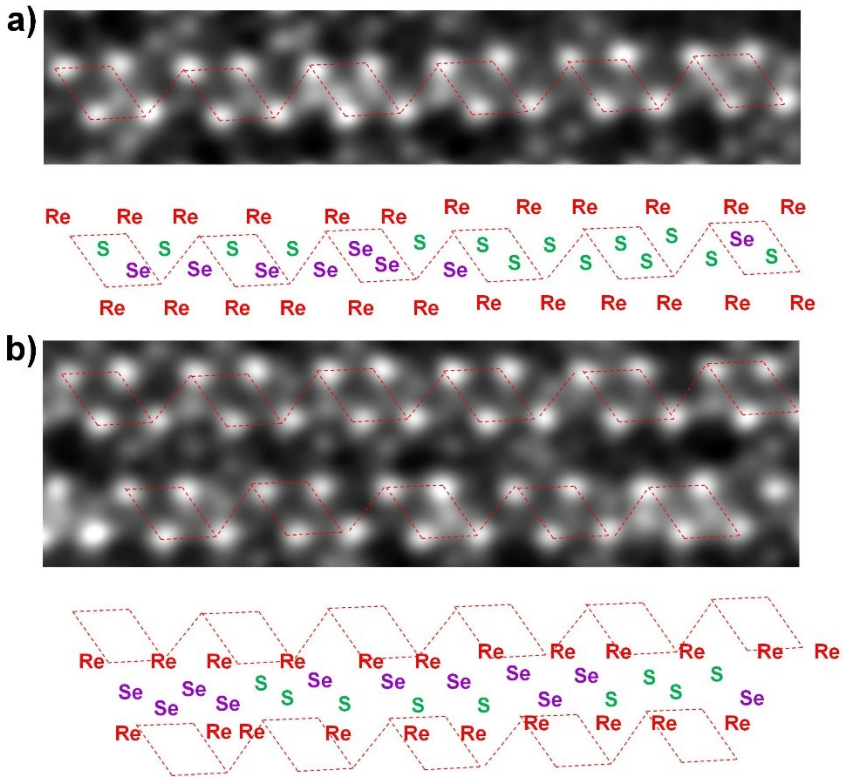

Fig. S1. (a) STEM image of $ReS_{1.4}Se_{1.6}$, showing a Re4 atomic chains and local atomic coordination structure. (b) STEM image and local coordination structure.

Supporting Note S1. Details on data analysis and image processing.

To extract the S/Se concentration at different atomic coordination sites, we carried out data analysis and image processing on different STEM images. The preliminary images were firstly filtered using Image J software for displaying clear atomic position.The data analysis was performed using a custom-written Matlab (MathWorks) code. The flow diagram of the analysis process is presented in Fig. S(2). After the loading of STEM image, which was firstly filtered by Image J. We can set the x, y range of the region we want to do the analysis. Then, we input the lattice parameter of *a*, *b*, the Theta between the *a* and *b* axis and the tilt angle of image. We can compare the lattice identification results on a Figure window in Matlab to check the precise of lattice generation. The main function for determining the lattice is shown as following:

```
function [ x_position,y_position, number_index, number_estimated
,a_vector,b_vector, x_position_ideal,y_position_ideal] =
STEM_analysis_lattice_generate_direct( a,b,theta,tilt_angle,x0,y0,xmax,ymax )
widthmax=max((ymax-y0),(xmax-x0));
number_estimated=(ymax-y0)*(xmax-x0)/a/a/sin(theta/180*pi);
number_index=0;
column_number=round(1.1*(round(sqrt((widthmax)^2+(widthmax)^2)/min(a,b))+1));
for p=0:column_number %a, hirozotal
for q=0:column_number %b, vertical
xy_distance=sqrt((p*a)^2+(q*b)^2-2*cos(pi-theta/180*pi)*a*p*b*q)
if p~=0
       theta_to_x_axes=tilt_angle/180*pi+acos(((p*a)^2+xy_distance^2-
(q*b)^2)/2/xy_distance/p/a)
elsetheta_to_x_axes=(theta+tilt_angle)/180*pi
end
x_temp=round(x0+xy_distance*cos(theta_to_x_axes));
y_temp=round(y0+xy_distance*sin(theta_to_x_axes));
if p==0 & q==0
number_index=1;
x_position(number_index,1)=x0;
y_position(number_index,1)=y0;
a_vector(number_index,1)=0;
b_vector(number_index,1)=0;
x_position_ideal(number_index,1)=x_temp;
y_position_ideal(number_index,1)=y_temp;
else
```

```
p
q
x_temp
y_temp
if (x_temp<=xmax&x_temp>=x0-1 &y_temp<=ymax&y_temp>=y0-1);
number_index=number_index+1;
x_position(number_index,1)=x_temp;
y_position(number_index,1)=y_temp;
a_vector(number_index,1)=p;
b_vector(number_index,1)=q;
x_position_ideal(number_index,1)=x_temp;
y_position_ideal(number_index,1)=y_temp;
end
end
end
end
```

In the analysis, we did not use the lattice generated by the first step directly, but searched a maximum intensity in the region near the generated position as the practical Re position and the detailed function is:

```
function [  x_position_1D,y_position_1D] =
STEM_analysis_lattice_generate_search(
image_data,x_position_1D,y_position_1D,ROI,int_range_min,int_range_max,min_p
ixel );
number_index=size(x_position_1D);
for i=1:number_index
ROI_array=image_data((y_position_1D(i)-
ROI):(y_position_1D(i)+ROI),(x_position_1D(i)-ROI):(x_position_1D(i)+ROI));
             [ROI_1D_max ROI_y_position_line]=max(ROI_array);
             [ROI_2D_max ROI_x_position]=max(ROI_1D_max);
ROI_y_position=ROI_y_position_line(ROI_x_position);

if ROI_2D_max<=int_range_max& ROI_2D_max>=int_range_min

                x_position_1D(i)=x_position_1D(i)+ROI_x_position-ROI;
                y_position_1D(i)=y_position_1D(i)+ROI_y_position-ROI;
end
end
```

As shown by the codes highlighted in blue, we carried out a searching process near the position of lattice and determined a point with maximum intensity as the

position of Re atom, which can eliminate the deviation between the standard $ReS_{2(1-x)}Se_{2x}$ lattice and practical STEM image. After the determination of the lattice, we set the offset values for S/Se sites compared with the pristine Re position in each unit cells. Next, we searched a maximum value near the firstly determined S/Se coordination sites as the intensity of the sites and the main function is shown as follow:

```
function [ atomassign_result , max_int_array] =
STEM_analysis_atom_assignment(atomassign_result,image_data,atom_site_x,atom_
site_y,atomassign_site_selected,atomassign_ROI,atomassign_min,atomassign_max,a
tomassign_atom_name, atom_number );
%UNTITLED1 Summary of this function goes here
%  Detailed explanation goes here
[n, m]=size(atom_site_x)
x_position=atom_site_x(1:atom_number,atomassign_site_selected);
y_position=atom_site_y(1:atom_number,atomassign_site_selected);
max(x_position)
min(x_position)
max(y_position)
find(y_position==1500)
for i=1:atom_number
ROI_array=image_data((y_position(i)-
atomassign_ROI):(y_position(i)+atomassign_ROI),(x_position(i)-
atomassign_ROI):(x_position(i)+atomassign_ROI),1);
   ave_int=sum(sum(ROI_array))/(2*atomassign_ROI+1)/(2*atomassign_ROI+1);
max_int=max(max(ROI_array));
max_int_array(i)=max_int;
ifmax_int<=atomassign_max&max_int>=atomassign_min
      atomassign_result(i,atomassign_site_selected)={atomassign_atom_name};
end
end

figure(2);
int_array=0:65535/255:65535;
hist(max_int_array,int_array);
```

As shown in the highlight part, we extracted the maximum value in the region of each coordination sites as the intensity, which ensures the accuracy of our analysis results. The numbers marked in the Fig. S4 and S5 is added by the set position according to the ideal lattice, since extract the position of maximum intensity requires additional codes, which is detrimental to the running speed.

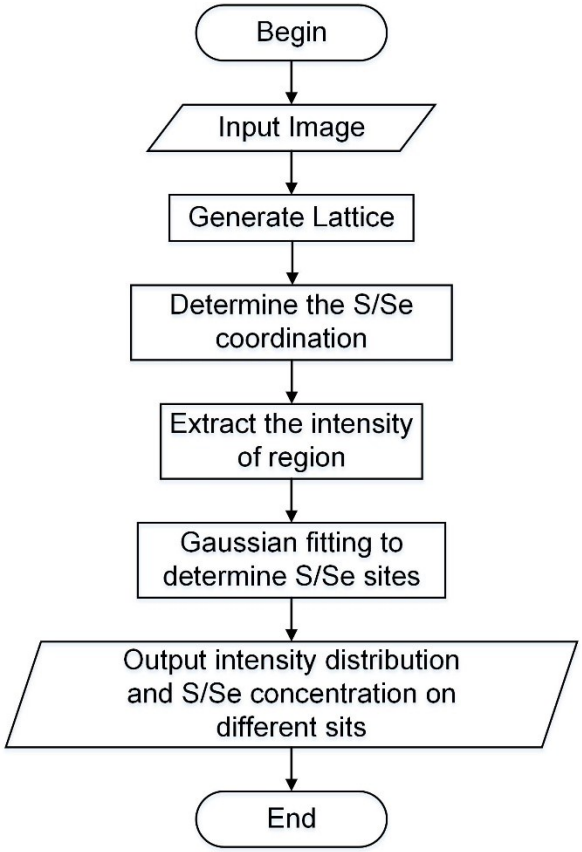

Figure S2. A flow diagram for analysis of S/Se coordination in STEM image.

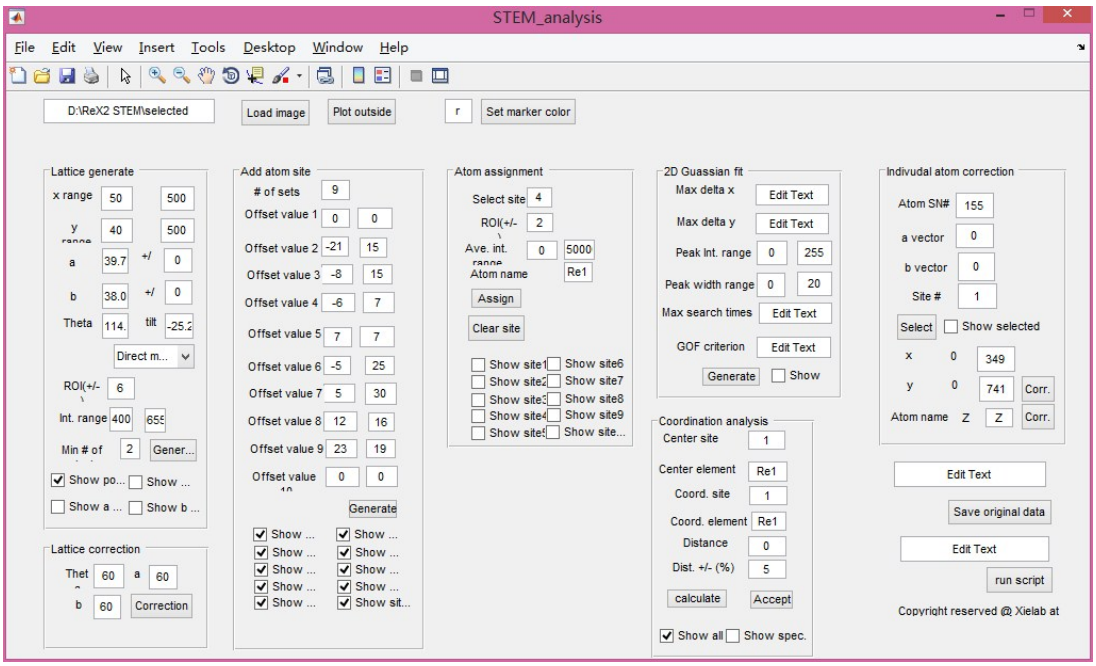

Figure S3. Matlab GUI of the STEM coordination analysis.

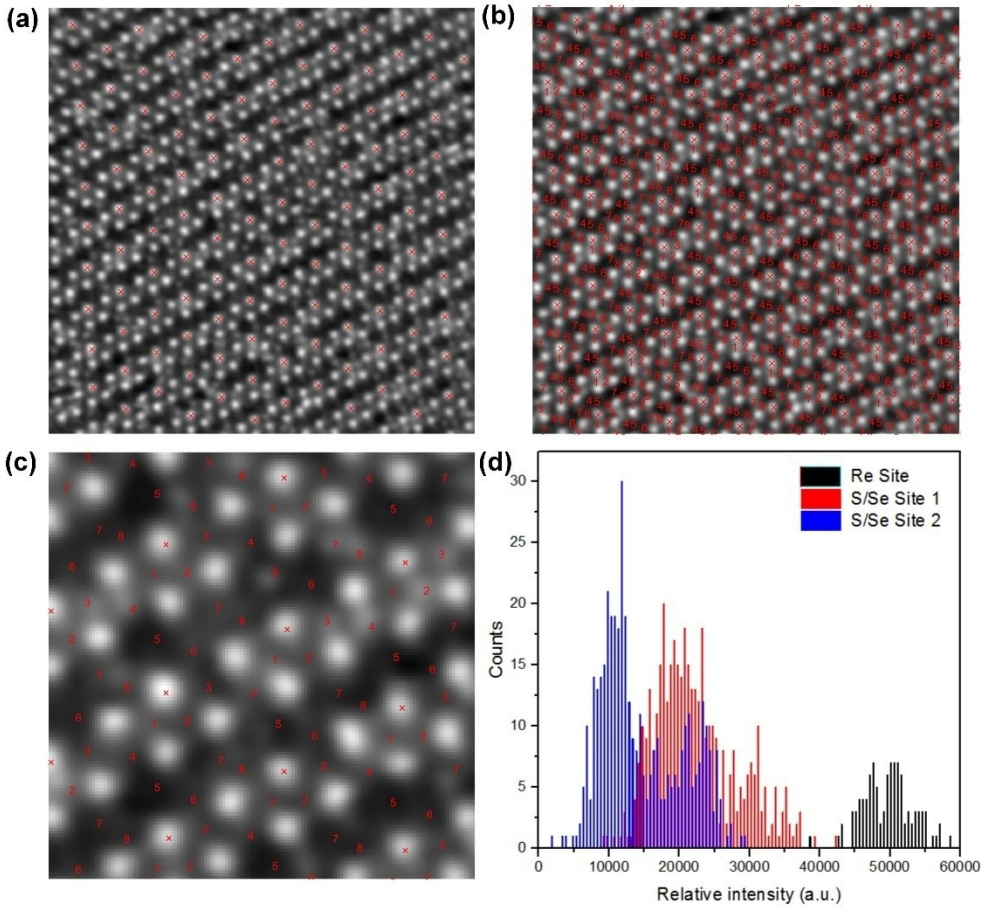

Fig. S4. The extraction of local coordination sites from STEM images.(a)STEM image with determined position of unit cells. The position of unit cell is marked with a red 'x' on a Re atom. (b) STEM image with atomic sites marked with different numbers that represents different coordination sites shown in Figure 3(a) in main text. (c) Zoom-in STEM image presents clear coordination sites. (d) The distribution of grey scale value at position of different sites, which illustrates an obvious contrast between S and Se atoms.

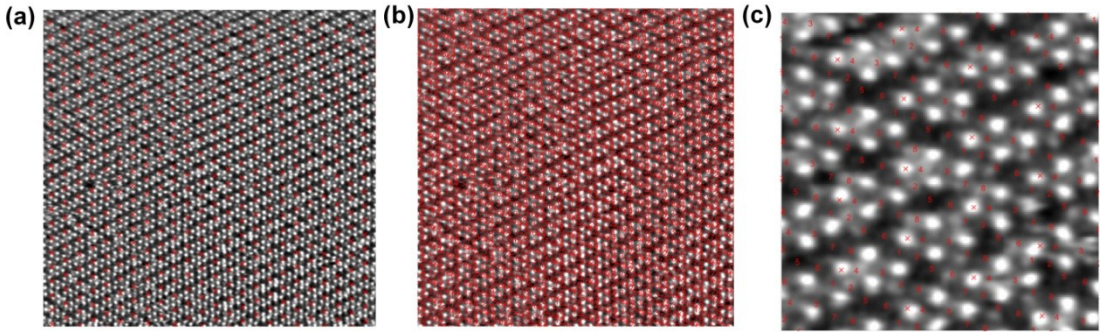

Fig. S5. Extraction of local atomic coordination at another STEM region. (a) STEM image with determined position and lattice parameter of unit cells. (b) STEM image with determined atomic sites. The different atomic coordination sites are marked with numbers of 1-8. (c) Zoom-in STEM images, presenting clear position of coordination sites. The distribution of grey values, that represents the intensity of sites, is presented in Figure 3(b). The concentration of S and Se atoms at different coordination sites can be extracted.

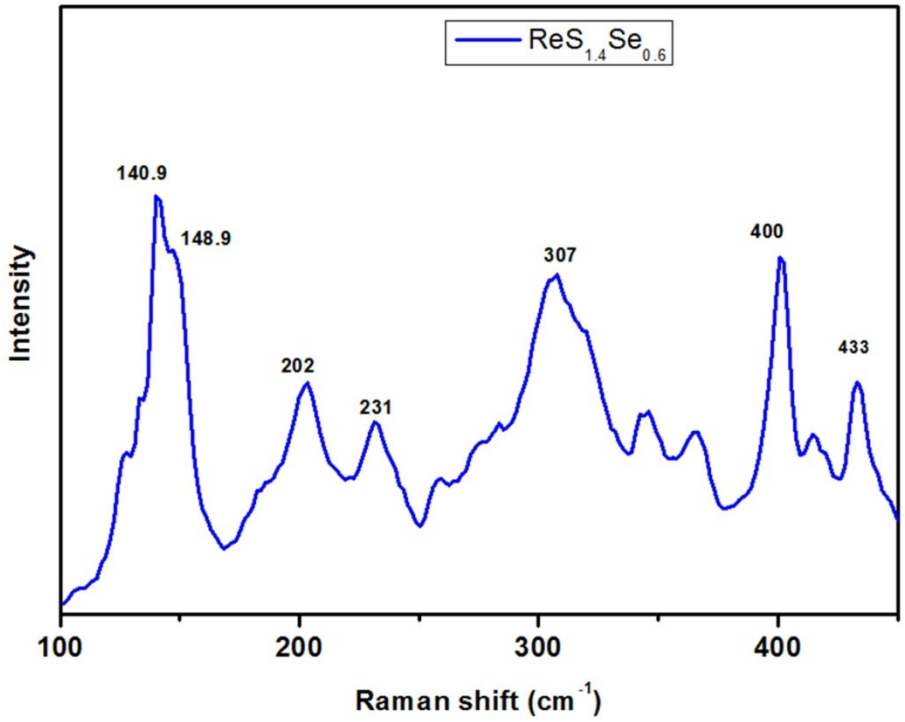

Fig. S6. Raman spectrum of monolayer $ReS_{1.4}Se_{0.6.}$

Supporting Note S2. Details on calculation on the relative occupation probability and Se percentage at growth temperature.

Since Se has different energy at different site, the relative occupation probability of Se at a specific site *i*, $P_{(\mathrm{Se},i)}$ can be calculated as

$$P_{(Se,i)} = \exp(\frac{-E_i}{k_B T})$$

where$E_{\mathrm{i}}$is the Se substitution energy at site *i*, k_{B} is the Boltzmann constant and *T* is the growth temperature (*T*=1303 K). From the calculated energy difference, the $P_{(Se,i)}$ can be calculated. Then Se percentage at different site,$Content_{(\mathrm{Se,i})}$, can be calculated by

$$Content_{(Se,i)} = \frac{P_{(Se,i)}}{(\sum_{1}^{8} P_{(Se,i)})/8} \bullet Content_{(Se,average)}$$

where$Content_{(\mathrm{Se},average)}$is the average Se content (0.30). According to the calculated results shown in Table S1, the probability of Se substitution of S at the growthtemperature is well consistent with experimental results.

Table S1. The calculated relative energy, relative occupation probability, Se percentage and experimental Se percentage.

Sites	Relative energy for Se substitution (eV) at room temperature	Calculated relative occupation probability, $P_{(\mathrm{Se},i)}$ at 1303 K	Calculated Se percentage at different sites, $Content_{(\mathrm{Se},i)}$ at 1303 K	Experimental Se percentage from STEM imaging at different sites (data derived from Fig. 3c)
1,2	0.057	0.602	0.217	0.212
3,4	0.026	0.794	0.287	0.279
5,6	0	1	0.362	0.363
7,8	0.009	0.923	0.334	0.319