

*- Supplementary Information -*

# Correlation of Grain Orientations and the thickness of Gradient MoS<sub>2</sub> films

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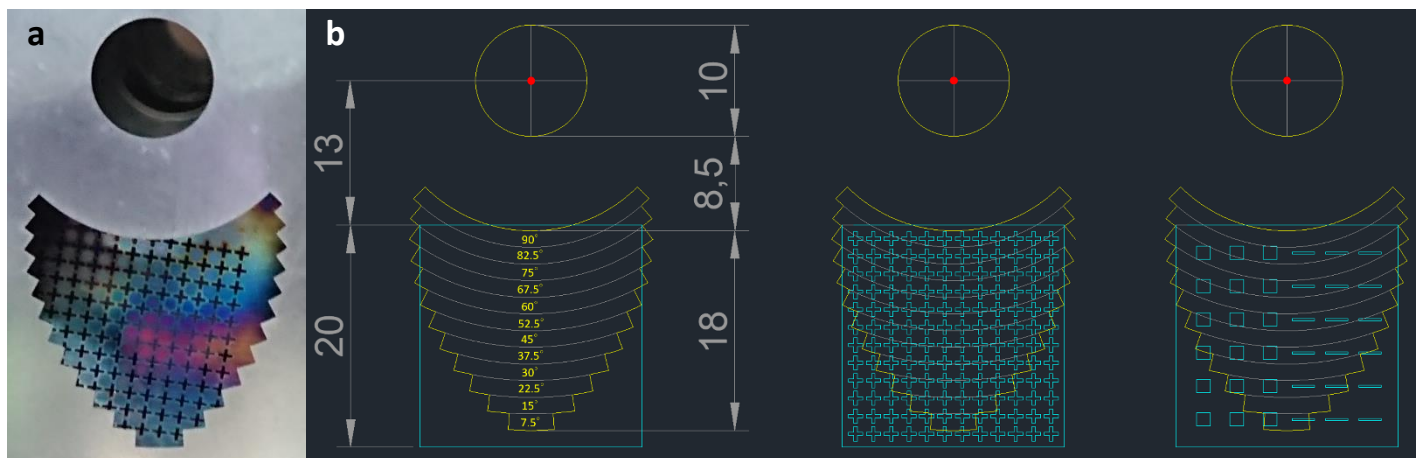
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## S1: Design of the gradient deposition



**Figure S1-1.** The full view of the suspended-gradient mask.



**Figure S1-2.** (a) The photograph of the suspended gradient mask (white) and the shadow mask (with color) attached on the substrate. (b) The illustration of masks. Yellow parts refer to the gradient mask, which is suspended and static during the deposition, while blue parts refer to the shadow masks attached on the substrate, which rotates around the red dot (the fixed center) during the deposition. The unit of length is millimeter.

## S2: Calculation of $t_{Mo}$ and $t_{MoS_2}$

According to Figure S1-1 and S1-2, the distance from the rotation center (red dot) determined the exposure time when applying the gradient mask during the deposition. Assuming the deposition rate without the gradient mask ( $t_0$ , which is measured by the thickness monitor in the evaporator) is uniform within a radius of 40 mm, and the distribution of the gradient deposition is linear from (0, -13.5) to (0, -31.5) and from 25 % to 0% of  $t_0$ , the thicknesses of Mo precursor ( $t_{Mo}$ ) can be determined by the position (x, y) with following equation:

$$t_{Mo}(x, y, t_0) = t_0 \times \left( 0.4375 - \frac{0.25}{18} \times \sqrt{x^2 + y^2} \right) \quad \text{when } 13.5 \leq \sqrt{x^2 + y^2} \leq 31.5$$

(1)

According to the polynomial function obtained from the results TEM images in Figure 2e:  $t_{MoS_2} = 0.22944 t_{Mo}^3 + 0.34549 t_{Mo}^2 + 2.74309 t_{Mo} - 0.01078$ , one can calculate the  $t_{MoS_2}$  value at any position. Table S2-1, S2-2 show the positions (x, y) of the Raman spots, and the corresponding values of  $t_{Mo}$  and  $t_{MoS_2}$ . Note that  $t_0$  in both tables is 16 nm.

**Table S2-1.** The positions (x,y) and the thicknesses ( $t_{Mo}$  and  $t_{MoS_2}$ ) of five TEM samples.

x (mm)	y (mm)	$t_{Mo}$ (nm)	$t_{MoS_2}$ (nm) (measured by TEM)
-1.5	-15.5	3.54	24.26
-1.5	-18.5	2.88	15.97
-1.5	-21.5	2.21	10.51
-1.5	-24.5	1.55	5.76
-1.5	-27.5	0.88	N/A

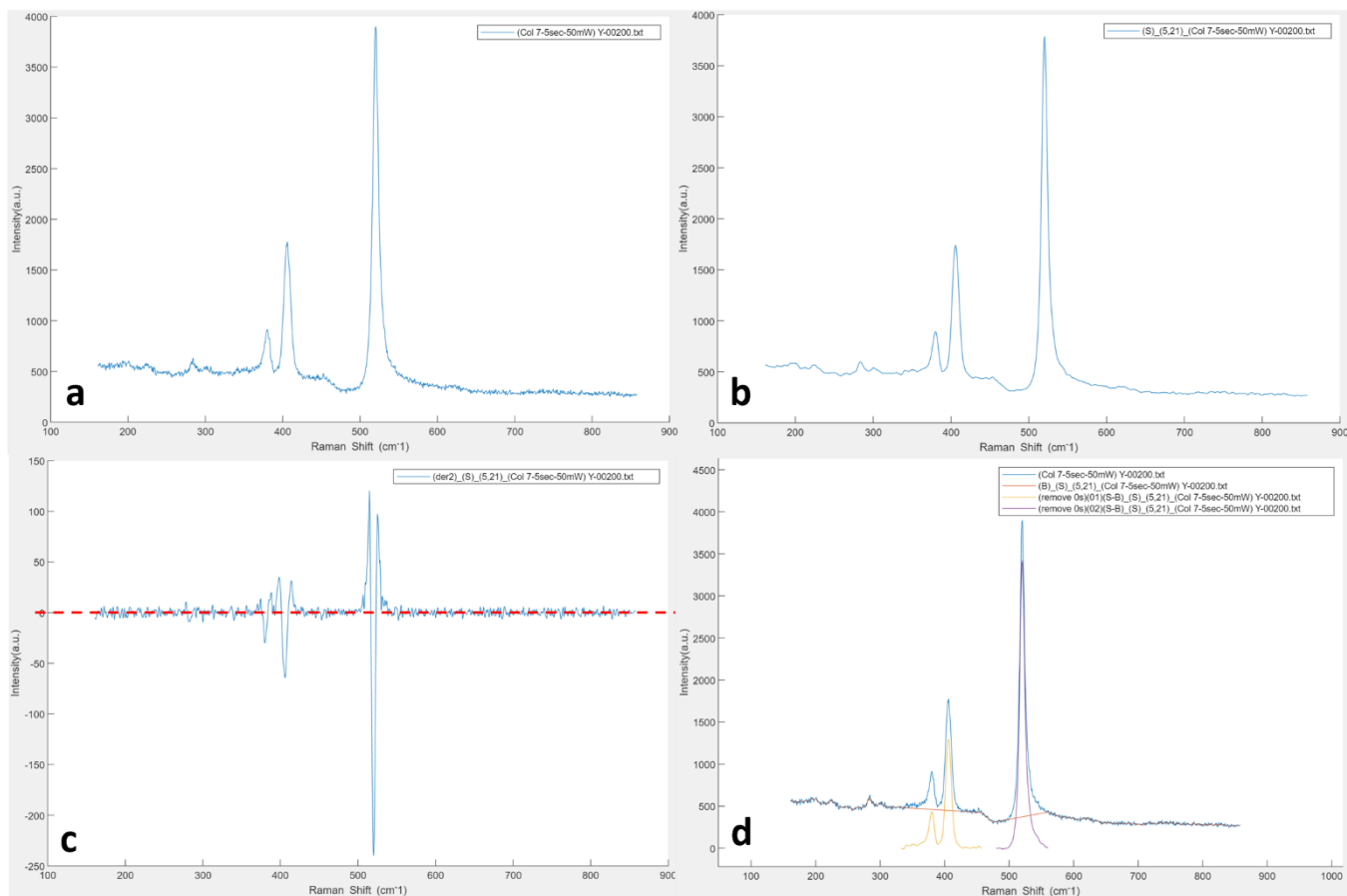
**Table S2-2.** The positions and the thicknesses ( $t_{\text{Mo}}$  and  $t_{\text{MoS}_2}$ ) of 19 sites for Raman measurement.

x (mm)	y (mm)	$t_{\text{Mo}}$ (nm)	$t_{\text{MoS}_2}$ (nm)	x (mm)	y (mm)	$t_{\text{Mo}}$ (nm)	$t_{\text{MoS}_2}$ (nm)
0.7935	-13.7	3.95	30.36	0.7935	-21.7	2.17	9.95
0.7935	-14.5	3.77	27.58	0.7935	-22.5	2.00	8.67
0.7935	-15.3	3.60	24.98	0.7935	-23.3	1.82	7.50
0.7935	-16.1	3.42	22.56	0.7935	-24.1	1.64	6.44
0.7935	-16.9	3.24	20.31	0.7935	-24.9	1.46	5.46
0.7935	-17.7	3.06	18.22	0.7935	-25.7	1.29	4.58
0.7935	-18.5	2.89	16.29	0.7935	-26.5	1.11	3.77
0.7935	-19.3	2.71	14.50	0.7935	-27.3	0.93	3.03
0.7935	-20.1	2.53	12.85	0.7935	-28.1	0.75	2.35
0.7935	-20.9	2.35	11.34				

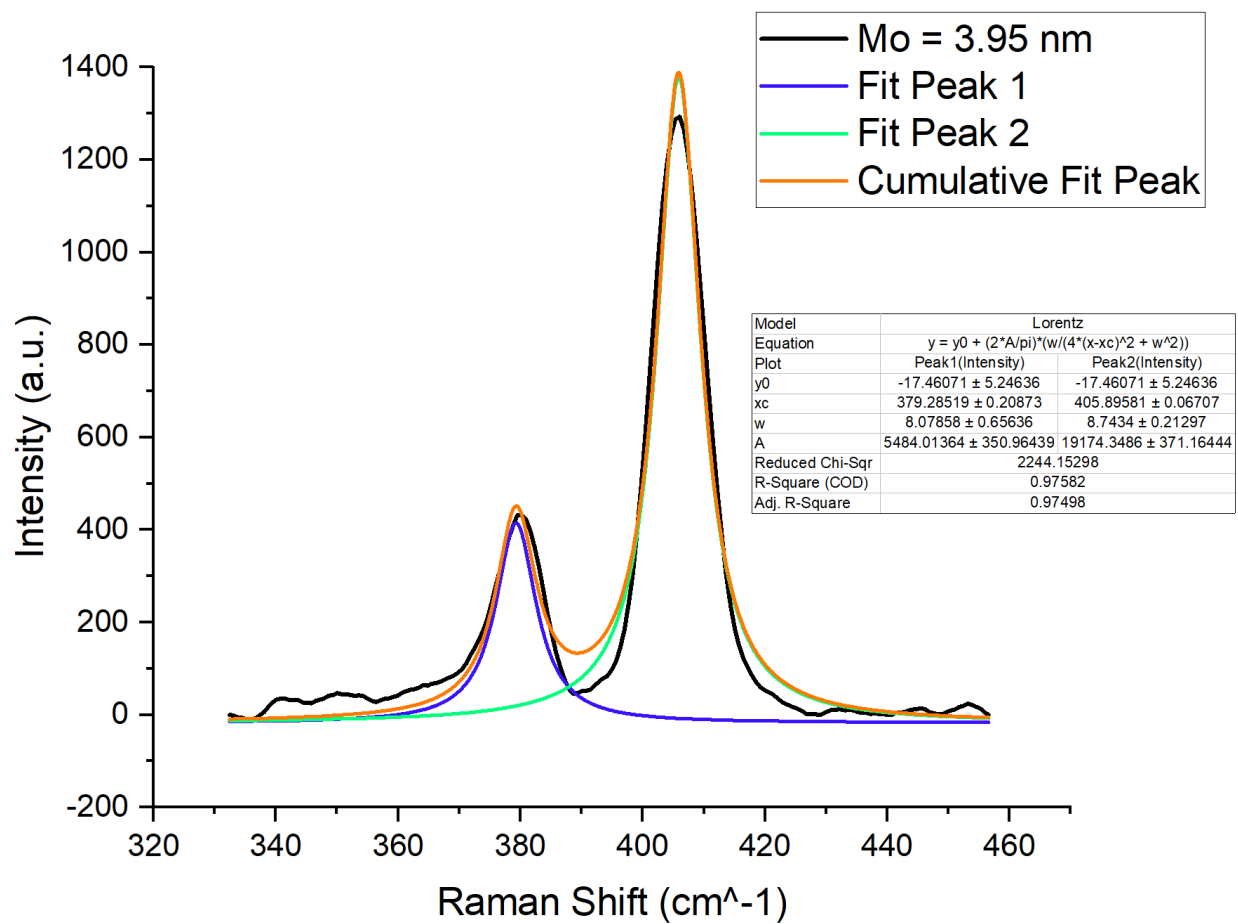
### **S3: Analysis procedures of Raman spectra**

We apply two Lorentzian functions to fit each spectrum by using Origin software. Before fitting, we selected the fitting range and removed the baseline by Matlab auto-program. The analysis procedures were adapted from the First-Derivative Method in ref [S1]. The steps of the analysis include:

- (1) Smooth the Raman spectrum by the Savitzky–Golay filter (Figures S2a and S2b).
- (2) Calculate the 2<sup>nd</sup> derivative of the spectrum. Estimate the peak width ( $w_{\text{est}}$ ) and the peak position ( $X_{\text{c}_{\text{est}}}$ ) by the 2<sup>nd</sup> derivative (Figure S2c).
- (3) Go back to the original spectrum. Select the spectrum in the range of ( $X_{\text{c}_{\text{est}}} - 10 w_{\text{est}}$ ,  $X_{\text{c}_{\text{est}}} + 10 w_{\text{est}}$ ). Eliminate the data outside the selected range. Remove the baseline which is linear and drawn from ( $X_{\text{c}_{\text{est}}} - 10 w_{\text{est}}$ ) to ( $X_{\text{c}_{\text{est}}} + 10 w_{\text{est}}$ ) (Figure S2d).
- (4) Fit the spectrum by Origin (Figure S3).



**Figure S2.** (a) Original spectrum. (b) The spectrum after smoothing. (c) Blue line: 2<sup>nd</sup> derivative of the smoothed spectrum. By comparing the 2<sup>nd</sup> derivative and the red dash line ( $y = 0$ ), one can estimate the peak width and the peak center. (d) Blue line: the original spectrum. Orange line: baseline. Yellow line and purple line: the extracted spectra after baseline removal.



**Figure S3.** Spectrum fitting operated with Origin software.

#### S4: Theoretical simulation of the intensity versus $\theta$

According to previous report<sup>23,25</sup>, the total scattering intensity (denoted as  $I$  in the following passages) of a vibrational mode can be calculated by the following equation:

$$I = \int_V \int_{\Omega} |\vec{E}_{in} \mathbf{R}_{xyz} \vec{E}_{sc}|^2 d\Omega dV \quad (2)$$

In Equation 2,  $\vec{E}_{sc}$  and  $\vec{E}_{in}$  are the vectors describing the electric field of scattering and incident light, respectively.  $\mathbf{R}_{xyz}$  is the Raman tensor matrix of the material in terms of the Cartesian coordination of substrate.  $\Omega$  is the solid angle of scattering cone.  $V$  is the total volume. Both  $\Omega$  and  $V$  depend on the numerical aperture of the objective lens (NA).

Equation 2 can be reduced as the following expression<sup>23, 25</sup>:

$$\begin{aligned} I &= \int_V \int_{\Omega} |\vec{E}_{in} \mathbf{R}_{xyz} \vec{E}_{sc}|^2 d\Omega dV \\ &= (R_{xx}^2 A + R_{xy}^2 A + R_{xz}^2 B) C_x + (R_{yx}^2 A + R_{yy}^2 A + R_{yz}^2 B) C_y \\ &+ (R_{zx}^2 A + R_{zy}^2 A + R_{zz}^2 B) C_z \end{aligned} \quad (3)$$

In Equation 3,  $R_{ij}$  ( $i = x, y, z ; j = x, y, z$ ) are the elements of  $\mathbf{R}_{xyz}$  matrix. A and B are coefficients related to the microscopes.  $C_x, C_y, C_z$  are coefficients proportional to the integrated intensities of  $E_{in, x}, E_{in, y}$  and  $E_{in, z}$ .  $(A, B) = (8.593, 5.111)$  for the numerical aperture of the objective lens (NA) being 0.9, and  $(C_x, C_y, C_z) = (13.722, 0.082, 2.192)$  for an X-polarized



incident laser [1]. In the simulation, we utilized  $(C_x', C_y', C_z') = (C_x + C_y, C_x + C_y, 2C_z)$  in Equation 3 for the coefficients of the non-polarized laser beam.

The Raman tensor matrix of  $A_{1g}$  and  $E_{2g}^1$  of  $\text{MoS}_2$  are:

$$\mathbf{R}_{xyz} = \mathbf{R}_1 \mathbf{R}_2 \mathbf{R}_3 \mathbf{R}_{xyz} \mathbf{R}_3^T \mathbf{R}_2^T \mathbf{R}_1^T \quad (4)$$

Where

$$\mathbf{R}_{xyz, A_{1g}} = \begin{pmatrix} 195 & 0 & 0 \\ 0 & 195 & 0 \\ 0 & 0 & 276 \end{pmatrix};$$

$$\mathbf{R}_{xyz, E_{2gx}^1} = \begin{pmatrix} 125 & 0 & 0 \\ 0 & -125 & 0 \\ 0 & 0 & 0 \end{pmatrix}; \quad \mathbf{R}_{xyz, E_{2gy}^1} = \begin{pmatrix} 0 & -125 & 0 \\ -125 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

and

$$\mathbf{R}_1 = \begin{pmatrix} c_1 & -s_1 & 0 \\ s_1 & c_1 & 0 \\ 0 & 0 & 1 \end{pmatrix}; \quad \mathbf{R}_2 = \begin{pmatrix} c_2 & 0 & s_2 \\ 0 & 1 & 0 \\ -s_2 & 0 & c_2 \end{pmatrix}; \quad \mathbf{R}_3 = \begin{pmatrix} c_3 & -s_3 & 0 \\ s_3 & c_3 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$(c_1, s_1, c_2, s_2, c_3, s_3) = (\cos \alpha, \sin \alpha, \cos \vartheta, \sin \vartheta, \cos \gamma, \sin \gamma)$$

$\alpha, \vartheta$  and  $\gamma$  are the Euler angles with  $\alpha = 0$  to  $2\pi$  and  $\gamma = 0$  to  $2\pi$  for each value of  $\vartheta$ . The

following script is the MATLAB code of this simulation:

```
% Raman tensor matrix
a=195;
b=276;
c=125;
A1g = [a 0 0; 0 a 0; 0 0 b];
E2gx = [c 0 0; 0 -c 0; 0 0 0];
E2gy = [0 -c 0; -c 0 0; 0 0 0];

% coefficients for the case of NA = 0.9 (θm = 64.2°)
A=8.593;
B=5.111;

% coefficients of an X-polarized laser beam
CC0=6.82;
```

```

CC1=0.548;
CC2=0.082;
x=2*CC0+CC2; y=CC2; z=4*CC1;

% {
transform the coefficients
to the case of the non-polarized laser beam
(equally polarized in x and y direction)
% }
x = x+y; y =x; z = z*2;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
d = pi/180; % degree
IA = [0 0];
IE1 = [0 0];
IE2 = [0 0];
for theta = 0:1:90
    IA(theta+1,1) = theta;
    IA(theta+1,2) = 0; % set the intensity = 0
    c2 = cos(theta*d); s2 = sin(theta*d);
    Rsum = [0 0 0; 0 0 0; 0 0 0];
    for alpha = 0:1:359
        c1 = cos(alpha*d); s1 = sin(alpha*d);
        for gama=0:1:359
            c3 = cos(gama*d); s3 = sin(gama*d);
            R1 = [c1 -s1 0; s1 c1 0; 0 0 1];
            R2 = [c2 0 s2; 0 1 0 ; -s2 0 c2];
            R3 = [c3 -s3 0; s3 c3 0; 0 0 1];
            Rtotal = R1*R2*R3*A1g*transpose(R1*R2*R3);
            Rsquare = Rtotal.* Rtotal;
            Rsum = Rsum + Rsquare;
        end
    end
    Rsum = Rsum / (360*360);

    IA(theta+1,2) = (Rsum(1,1)*A + Rsum(1,2)*A + Rsum(1,3)*B)*x...
        + (Rsum(2,1)*A + Rsum(2,2)*A + Rsum(2,3)*B)*y...
        + (Rsum(3,1)*A + Rsum(3,2)*A + Rsum(3,3)*B)*z;
end
for theta = 0:1:90

```

```

IE1(theta+1,1) = theta;
IE1(theta+1,2) = 0;% set the intensity = 0;
c2 = cos(theta*d); s2 = sin(theta*d);
Rsum = [0 0 0; 0 0 0; 0 0 0];
for alpha = 0:1:359
    c1 = cos(alpha*d); s1 = sin(alpha*d);
    for gama=0:1:359
        c3 = cos(gama*d); s3 = sin(gama*d);
        R1 = [c1 -s1 0; s1 c1 0; 0 0 1;];
        R2 = [c2 0 s2; 0 1 0 ; -s2 0 c2;];
        R3 = [c3 -s3 0; s3 c3 0; 0 0 1;];
        Rtotal = R1*R2*R3*E2gx*transpose(R1*R2*R3);
        Rsquare = Rtotal.* Rtotal;
        Rsum = Rsum + Rsquare;
    end
end
Rsum = Rsum / (360*360);
IE1(theta+1,2) = (Rsum(1,1)*A + Rsum(1,2)*A + Rsum(1,3)*B)*x...
    + (Rsum(2,1)*A + Rsum(2,2)*A + Rsum(2,3)*B)*y...
    + (Rsum(3,1)*A + Rsum(3,2)*A + Rsum(3,3)*B)*z;
end

for theta = 0:1:90
    IE2(theta+1,1) = theta;
    IE2(theta+1,2) = 0;% set the intensity = 0;
    c2 = cos(theta*d); s2 = sin(theta*d);
    Rsum = [0 0 0; 0 0 0; 0 0 0];
    for alpha = 0:1:359
        c1 = cos(alpha*d); s1 = sin(alpha*d);
        for gama=0:1:359
            c3 = cos(gama*d); s3 = sin(gama*d);
            R1 = [c1 -s1 0; s1 c1 0; 0 0 1;];
            R2 = [c2 0 s2; 0 1 0 ; -s2 0 c2;];
            R3 = [c3 -s3 0; s3 c3 0; 0 0 1;];
            Rtotal = R1*R2*R3*E2gy*transpose(R1*R2*R3);
            Rsquare = Rtotal.* Rtotal;
            Rsum = Rsum + Rsquare;
        end
    end
end
Rsum = Rsum / (360*360);
IE2(theta+1,2) = (Rsum(1,1)*A + Rsum(1,2)*A + Rsum(1,3)*B)*x...

```

```

+ (Rsum(2,1)*A + Rsum(2,2)*A + Rsum(2,3)*B)*y...
+ (Rsum(3,1)*A + Rsum(3,2)*A + Rsum(3,3)*B)*z;
end
IE = IE1+IE2;
IE(:,1) = IE(:,1) /2;
Ratio(:,1) = IA(:,1);
Ratio(:,2) = IA(:,2) ./ IE(:,2);

% plot the figures
subplot(1,2,1);
plot ( IA(:,1), IA(:,2), IE(:,1), IE(:,2));
axis([0 90 3E6 15E6]);
xticks(0:10:90);
yticks(3E6:1E6:15E6);
legend( 'A_1_g','E^1_2_g','Location','northwest');
xlabel('θ degree (°)');
ylabel('Intensity (a.u.)');
subplot(1,2,2);
plot ( Ratio(:,1), Ratio(:,2) );
axis([0 90 1.2 3.8]);
xticks(0:10:90);
yticks(1.2:0.2:3.8);
xlabel('θ degree (°)');
ylabel('Ratio (A_1_g / E^1_2_g)');
Ratio

```

## Reference

[S1] Schulze, G., Jirasek, A., Yu, M. M. L., Lim, A., Turner, R. F. B., & Blades, M. W.

Investigation of Selected Baseline Removal Techniques as Candidates for Automated

Implementation. *Applied Spectroscopy*, **2005**, 59(5), 545–574. DOI:

10.1366/0003702053945985