

Supporting Information

Charge Accumulation Resulted Metallization of II-VI Semiconductor (ZnX X=O, S, Se) Films Neighboring to Polar Liquid Crystal Molecules and Surface Plasmonic Response in Visible Region

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1, DFT calculation details

The crystal structure of ZnSe, ZnS, ZnO and GaAs are shown in Figure S1(a-d) respectively. Only ZnO is wurtzite structure and isotropic. The structural optimizations of the most stable geometries and charge distribution were calculated via the CASTEP [1,2] computation module based on DFT. We chose plane wave ultra-soft pseudopotential (PWPP), generalized gradient approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) approaches to take electronic effects into account. The cutoff energy was set as 440 eV for ZnSe and ZnS, 630 eV for ZnO, 450 eV for GaAs and k points were 8×8×8 for resultant continuity. We use a super cell contained with 2×2×2 primitive cells to calculate its related properties and shown in Figure S2 (a) for blended structure and Figure S2 (b) for wurtzite structure. After stable geometries operations, the crystal lattice a are shown in Table S1. We set ZnSe as the sample for band structure (Figure S2 c) in brief. The band structure shows that the band gap $E_g=2.34$ eV for ZnSe, which is correct compared with previous works.

Traditionally, the permittivity could be expressed as:

$$\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2 \quad (\text{E1})$$

With DFT approach, the wave function could be achieved and more properties could be calculated based on that. For example, the permittivity is determined as general expression of the complex dielectric tensor [62]. The imaginary part is:

$$\varepsilon_2(\omega)_{\alpha\beta} = \frac{4\pi^2 e^2}{m^2 \omega^2} \sum_{i,f} \int \langle f | p_\alpha | i \rangle \langle i | p_\beta | f \rangle W_i (1 - W_f) \delta(E_f - E_i - \hbar\omega) d^3k \quad (\text{E2})$$

Here $\langle f | p_\alpha | i \rangle$ and $\langle i | p_\beta | f \rangle$ are dipole matrix elements. W_i is the Fermi distribution function

centered at E_i . α and β are one of the axes in space (x, y and z), respectively, for the cell. For example, ϵ_{xx} is the permittivity of ZnSe when electric field is along the x axis. But ZnSe is isotropic and the permittivities are the same with different axes. The real part $\epsilon_1(\omega)$ is achieved from $\epsilon_2(\omega)$ using the Kramers-Kronig relation in the form:

$$\epsilon_1(\omega)_{aa} = 1 + \frac{2}{\pi} P \int_0^{\infty} \frac{\omega' \epsilon_2(\omega')_{aa}}{\omega'^2 - \omega^2} d\omega' \quad (E3)$$

But for ZnO, the optical properties are isotropic, meaning $\epsilon_{xx} = \epsilon_{yy} \neq \epsilon_{zz}$. In **Generalization to Metallization in Other II-VI Semiconductors** section, ϵ_{xx} are applied to display the variation with charge accumulation density. The imaginary parts variation of ZnS, ZnO and GaAs are shown in Figure S3, corresponding to Figure 6 in main text. With charges modulation, there is a absorption peak in visible region for all materials, indicating the metallization in visible region.

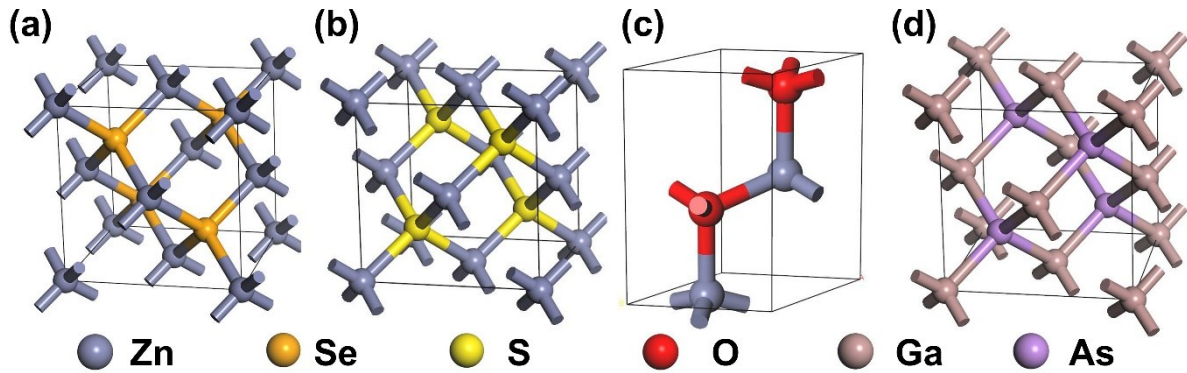


Figure S1. Crystal structure for ZnSe, ZnS, ZnO and GaAs, respectively.

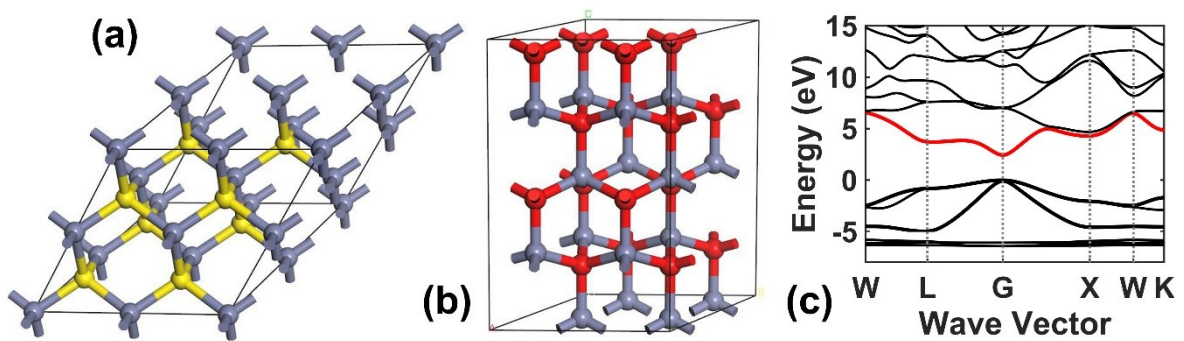


Figure S2. Calculated super cell for blende (a) and wurtzite (b) structure. (c) band structure of ZnSe.

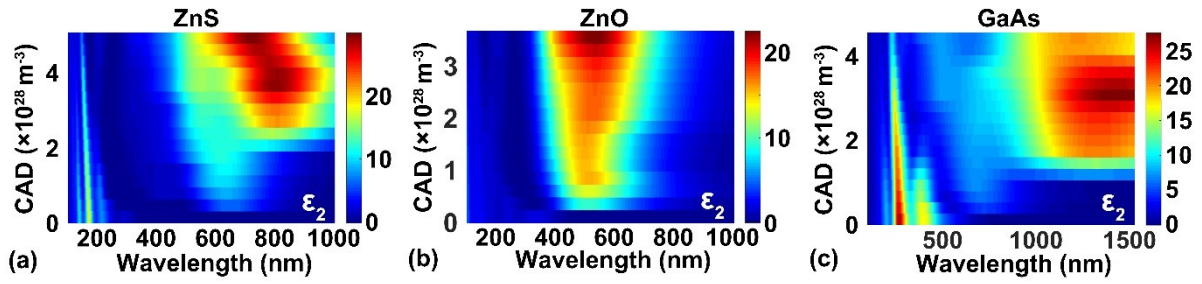


Figure S3. Imaginary part variation with CAD for (a) ZnS, (b) ZnO and (c) GaAs, corresponding to real part in Figure 6.

Table S1 Calculated crystal lattice

Lattice [\AA]	ZnO	ZnS	ZnSe	GaAs
α	3.251	5.419	5.737	5.716
c (wurtzite)	5.281	-	-	-

References

- [1] M. D. Segall, P. J. Lindan, M. A. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, M. C. Payne, *Journal of Physics: Condensed Matter*, **2002**, *14*, 2717.
- [2] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. Probert, K. Refson, M. C. Payne, *Zeitschrift für Kristallographie-Crystalline Materials*, **2005**, *220*, 567.