Supplemental Material : First-principles study on negative-U behavior of K centers in amorphous Si_3N_{4-x}

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MULTIPHONON-ASSISTED TUNNELING OF 1-D METAL-INSULATOR INTERFACE MODEL

To investigate the transition mechanism during charge injection into K center of a-Si_3N_4, we studied the charge trapping at the 1-D metal-insulator interface model. For the multiphonon-assisted tunneling, we referred to the formalism developed in ref.[1, 2]. The schematic of the device system we modelled is shown in Fig. S1 and the physical parameters are compiled in Table S1.

The defect depth (E_D) is the average thermodynamic transition level wherein atomic positions are fully relaxed under the new charge state. In Table S1, we used values for the Huang-Rhys (HR) factor and phonon energy that were found for point defects in semiconductors.[3, 4] The governing equation for the transition rate (R) is as follows,

$$R = \sum_{p\leq 0}^{-\infty} c_0 N_E(E_p) f(E_p) T_{ED}(E_p) L_p(z) e^{\frac{p\hbar\omega}{k_B T}} + \sum_{p>0}^{\infty} c_0 N_E(E_p) f(E_p) T_{ED}(E_p) L_p(z), \tag{S1}$$

where the c_0 is coefficient determined from the defect potential, of which we assumed delta-like shape, N_{E} is the density of states in the electrode, f is the Fermi-Dirac distribution, T_{ED} is tunneling coefficient evaluated within WKB approximation, E_p ($=E_D + p\hbar\omega$) is the energy of tunneling electron, and L_p is multiphonon transition probability given by

$$L_P(z) = \left(\frac{f_{BE}+1}{f_{BE}}\right)^{p/2} e^{-S(2f_{BE}+1)} I_p(z), \tag{S2}$$

where f_{BE} is the Bose-Einstein distribution, z is $2S[f_{BE}(f_{BE}+1)]^{1/2}$, and I_p is the modified Bessel function. The term with $p = 0$ (meaning that phonon mode of the trap site does not change) in the equation corresponds to the elastic transition, and the sum of the transition rate with $p \neq 0$ is inelastic transition. In evaluating the thermodynamic transition level, the atomic positions are in the respective ground states, which means that the phonon mode does not change, corresponding to the elastic transition. On the other hand, in the Franck-Condon (FC) or frozen-atom approximation, the atomic positions are in the excited phonon state and the number of phonons involved during the transition is $\sim S$ (and the phonon energy of the trap site becomes $\sim S\hbar\omega$ right after tunneling).

Figure S2 is the total transition rate evaluated by Eq. (S1) as a function of applied voltage. The elastic transition mainly occurs around 1.50 V/nm (voltage at which the trap level is placed ~0.3 eV below the Fermi level of the

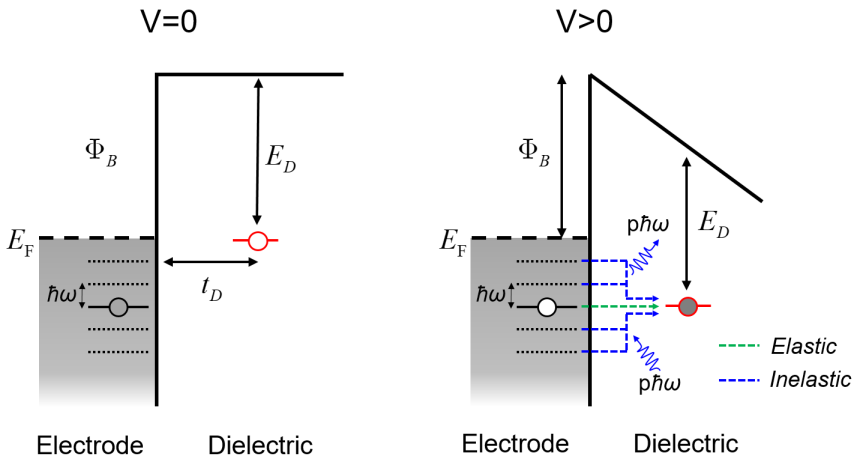

FIG. S1. Schematic diagram of 1-D metal-insulator interface model with a defect.

TABLE S1. Physical paramters used in the modeling of the 1-D metal-insulator interface.

Paramter	Value
Defect distance (t_D)	1 nm
Defect depth (E_D)	2.0 eV
Barrier height (Φ_B)	3.2 eV
HR factor (S)	15
$\hbar\omega$	0.04 eV
c_0	3.62E-33

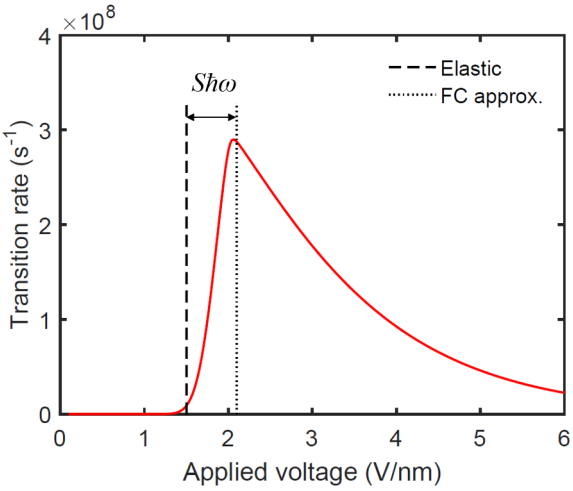

FIG. S2. Total transition rate calculated with sweeping applied voltage.

electrode). If only the FC approximation is assumed, the injection voltage will be 2.10 V/nm, because the trap level should be placed $\sim S\hbar\omega$ (= 0.60 eV) above the level in which elastic transition occurs (or E_D). In our result, the overall transition rate peaks at 2.06 V/nm, which is close to the injection voltage under FC approximation. To illustrate the contribution of elastic and inelastic transition more clearly, we plotted the transition rate with different number of phonons at 2.06 V/nm in Fig. S3.

It is shown that the transition rate peaks at around $p = 16$, which is close to the HR factor and so implies that the transition well correspond to the classical FC approximation.

While the detailed injection level would require the realistic device model considering the statistical variations found in this work, the above analysis implies that the trap level estimated by the FC approximation, rather than

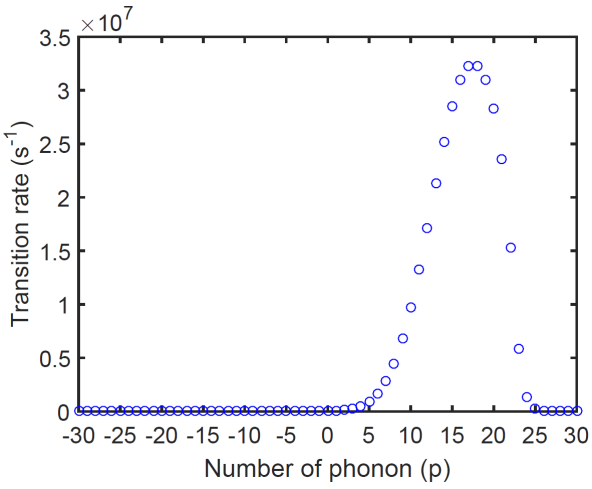

FIG. S3. Partial transition rate calculated with different number of phonons at 2.06 V/nm.

the fully-relaxed thermodynamic transition level, well corresponds to the trap level of a-Si_3N_4.

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