An analytic approach to the degradation of double-Schottky barrier: Theoretical prediction of $V_O^0-Zn_i^{2+}:Zn_i^{2+}$ as dominant mobile ion in ZnO electroceramic

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An analytic approach, aimed at characterizing the degradation properties of the double-Schottky barrier formed at the grain boundary in various electroceramics, is exhaustively described. Migration and neutralization behavior of charged defect ions is portrayed during the degradation of electrostatic potential under electrical stress. By comparing simulation results with experimental data from the aging test performed on fabricated $[0\,0\,0\,1]$ ZnO bicrystals, Zn_i^{2+} from $V_O^0-Zn_i^{2+}$ complex donor defect is identified as the optimum candidate for the mobile ion responsible for degradation phenomena of ZnO electroceramics.
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Double-Schottky barriers (DSBs), formed along the grain boundaries in various polycrystalline compound semiconductors such as ZnO, BaTiO₃, and SrTiO₃ [1,2] are responsible for their unique properties for commercial applications. However the degradation of the DSB under electrical stress is hazardous to electroceramic-based devices and thus become the focus of considerable interest. For the ZnO-based electroceramic [3], which is the vital protection component as a surge arrester in the energy transmission system and the electronic industry, it has been proved experimentally by the present authors [4] that the migration and neutralization of charged ions in the DSB region acts as the leading cause of electrical degradation. However, the lack of the identification and quantification of the dominant defect as a mobile ion has still complicated the elucidation of accurate physical processes governing the electrical degradation of DSB [5].

It is generally accepted that the negative acceptor-like interfacial states at the grain boundary (e.g. the principal acceptor V_{Zn} [6]) that are critical for the formation of DSB are spatially immobile [6–8], and the degradation of DSB can be mainly ascribed to the transition and motion of donor defects inside depletion layers. In the past nearly 4 decades, oxygen vacancy (V_O) and zinc interstitial (Zn_i) have been considered by researchers working on ZnO varistor as the dominant mobile donor ions [3,6]. This is strongly argued by numerous reports on experimentally

observed relaxation peaks corresponding to thermal transitional energy level at ~ 0.05 and ~ 0.20 eV below the conduction band minimum (CBM) within the facilitation of techniques like broadband dielectric spectroscopy and deep-level transient spectroscopy [9–11]. However, such beliefs must be re-examined, which is motivated by the fact that recent achievements in atomic-scale investigations on periodic-structure ZnO system using *density functional theory* calculations [12–17] have brought to our attention biased and distinct insight into the properties of native point defects in ZnO. Due to the different parameters used for calculations, e.g. exchange-correlation approximation, number of k-point samplings for Brillouin zone integration, supercell size, corrections for spurious image defect interactions, and so forth, predictions on characteristics of defects by various groups could certainly show disparities, whereas important and profound conclusions can still be extracted [18]. For instance, V_{Zn} is the lowest-energy acceptor which is in well conformity with previous discussion on the interfacial states. However, V_O, which is the lowest-energy donor defect and can be generated in large concentration, is surprisingly found to be a deep donor, i.e. its $(2+/0)$ transitional level lies ~ 1 eV below the CBM and V_O at $1+$ charge state is unstable [12,14,16]. Moreover, the formation energy of the shallow-donor Zn_i is much higher compared to V_O, and the low migration energy barrier for individual Zn_i around 0.5 eV (both calculated and experimental value) [16] indicates that the Zn_i defect becomes mobile at low temperature (~ 219 K), even though its thermal $(1+/0)$ and $(2+/1+)$ transitional levels are predicted as 0.05 and

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0.16 eV below the CBM by Vidya [12], and as ~0.05 and 0.1 eV by Oba [19]. These predictions [5,6,20] strongly violate the belief of V_O or Zn_i as the dominant mobile ion responsible for degradation phenomena, and significantly complicate and impede the clarification of a precise mechanism for DSB degradation.

In effect, if the species of the mobile ions can be determined, specific measures can be adopted to effectively prolong the service life of the devices. Owing to that traditional experimental techniques for characterizing the degradation of materials center on the measurement of apparent parameter variations rather than finding out the inherent changes, many of the fundamental degradation mechanisms are poorly understood. In this paper the long-term aging simulation, aimed at characterizing the degradation properties of individual grain boundaries which relies on portraying the migration and neutralization process of charged defect ions in the DSB region, is conducted with calculated results indicating that the Zn_i^{2+} from the complex donor defect (V_O^0–Zn_i^{2+}) is the optimum candidate for mobile ions.

To gain an insight into the degradation process and to determine the species that is most likely to be the mobile ion, a long-term aging simulation method based on Blatter and Greuter's model [21] (Fig. 1(a)) is presented. It should be noted here that, as seen in Figure 1(a), two
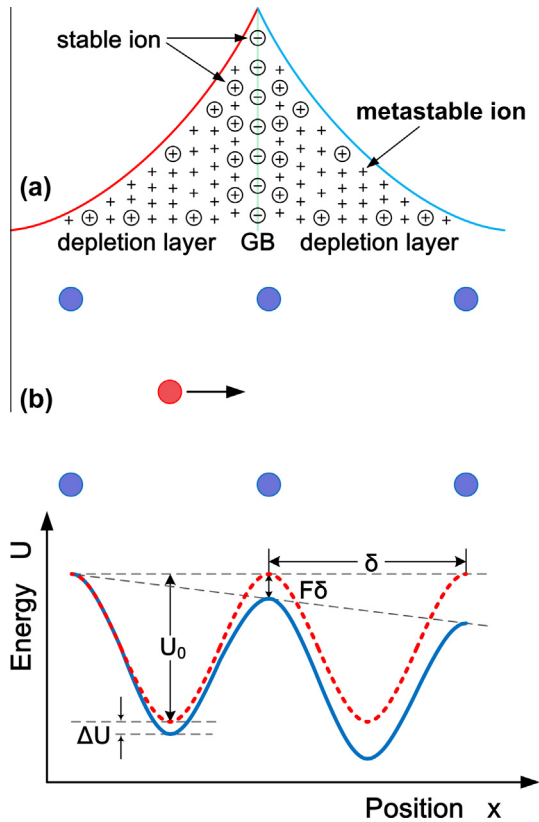

Figure 1. (a) DSB model based on charged defect ions. And (b) the migration of defect ion is exemplified by the motion of an interstitial ion (the blue balls represent periodic lattice sites while the red ball is the interstitial ion). Correspondingly, the migration energy barriers for the interstitial defect are illustrated for both with (solid line) and without (dash line) external electrical field cases (force F is equivalent to qE). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

types of positively charged donor defects exist in the depletion layer: one is the stable donor ion which along with the negative interfacial states is spatially fixed, and the other is the meta-stable species that can be perturbated by an external electric field and migrate to the grain boundary [6]. However, for the simplicity of theoretical modeling, the depletion layer is assumed to be populated with meta-stable donors only in the following simulation. According to the Boltzmann statistics, ΔP, the net migrating rate of ions along the direction of the applied electric field, is

$$\Delta P = \frac{\gamma_0}{6} \exp(-U_0/kT)[\exp(+\Delta U/kT) \\ - \exp(-\Delta U/kT)] \tag{1}$$

where k is the Boltzmann constant, T is the temperature, γ_0 is the vibration frequency of the ion at semi-stable position, U_0 is the migration barrier along the saddle point without applied voltage, and ΔU is the potential difference caused by the electric field $\Delta U = qE(x,t) \cdot \delta/2$ (δ is the distance between adjacent semi-stable positions, and q is the charge of ion) as seen in Figure 1(b). The migration velocity of the ion is $v = \Delta P \cdot \delta$. Based on the discussion by Blatter and Greuter [21], the distribution of electric field $E(x,t)$ in the DSB region and further the Schottky barrier geometry $\phi(x,t)$ can be obtained by the numerical integration technique with confining the Poisson's equation as $\phi(-\infty) = \phi(-x_{l0}) = 0$ and $\phi(+\infty) = \phi(x_{r0}) = -V$, where x_{l0} and x_{r0} are the widths of the depletion layers on both sides of the grain boundary and V is the applied voltage. The Poisson's equation is given below:

$$\frac{d^2\phi(x,t)}{dx^2} = -\frac{e \cdot \rho(x,t)}{\varepsilon_0 \varepsilon_r} \tag{2}$$

where e is the elementary charge, ρ is the spatial distribution of charge, ε_0 is the permittivity of vacuum and ε_r is the dielectric constant. The discretization procedures for Poisson's equation are narrated in Supplementary materials [22]. For $\rho(x,t)$ in Poisson's equation that is the critical component, the negative interfacial states are represented by $-Q_i\delta(x)$ at $x = 0$ where Q_i is the interface charge and $\delta(x)$ is the Dirac function, and as for the donor defects in both depletion layers, 4 hypothetical kinds of charged donor distributions (step, ramp, quadratic and exponential functions) as exemplified in Figure 2 are employed, which are appropriately set to ensure the equivalence of the initial current [23]. The relationship between grain boundary loss current and barrier height ϕ_B ($= \phi(x = 0)$) is:

$$j(t) = A^* T^2 \exp\left[-\frac{e\phi_B + \varepsilon_\xi}{kT}\right]\left[1 - \exp\left(-\frac{eV}{kT}\right)\right] \tag{3}$$

where A^* is the Richardson constant, and ε_ξ represents the Fermi level of grain boundary relative to the CBM. The initial current can be calculated by employing the initial barrier height before degradation in formula (3). Then the advection equation, which is frequently used for describing the diffusion process, is utilized to characterize the migration of donor defects:

$$\frac{\partial\rho(x,t)}{\partial t} + \frac{\partial[\rho(x,t) \cdot v(x,t)]}{\partial x} = 0 \tag{4}$$

The initial distribution of charged ions is considered as the starting condition for the advection equation. The part of ions migrating to and entering the interface would