

## ABSTRACT

A review is presented of the main ideas and applications to elemental and compound materials of the nanoscopic electron-affected stochastic dynamics of atomic diffusion in solids. This consideration is based on the stochastic kinetic many-body theory of nanoscopic picosecond short-lived large energy fluctuations (SLEFs) of atomic particles and SLEF-induced rate processes in solids. The SLEFs of lifetime  $\Delta\tau=10^{-13}-10^{-12}$  s supply strongly fluctuating hopping atoms (HAs) with the thermal energy  $\epsilon_{op} \geq \Delta E \gg kT$  sufficient to initiate diffusion events of duration  $\Delta\tau_d \approx \Delta\tau$ . The following main ideas are put in the foundations of the theory of SLEF-induced atomic diffusion in solids. (i) The energy is transferred in the lattice with the finite velocity  $c_s$  of the order of the sound velocity. (ii) The SLEF lifetime  $\Delta\tau=\tau_1+\tau_2$  and duration of a diffusion event  $\Delta\tau_d \approx \Delta\tau$  are short and include the SLEF formation time  $\tau_1 \approx 0.5\Delta\tau$  and SLEF relaxation time  $\tau_2 \approx \tau_1$ . (iii) Single picosecond SLEF-induced diffusion events obey the causality principle which determines the radius  $R_1 \approx c_s \tau_1 \approx 10^{-7}$  cm (or  $R_2 = c_s \tau_2 \approx R_1$ ) of the nanometer HA vicinity involved directly in the formation (relaxation) of the diffusion event during  $\tau_1$  (or  $\tau_2$ ) where  $\tau_1$  (and  $\tau_2$ ) depends on  $\epsilon_{op}$ , the coordination number  $z$  and the Debye temperature. (iv) The SLEF-induced diffusion jump of a single HA is a local non-equilibrium nanoscopic picosecond many-body phenomenon requiring the kinetic consideration. (v) The SLEF-induced single diffusion events are associated with the formation of large transient atomic displacements (LTADs) and transient (picosecond) point dynamic defects (TPDDs) of lifetime  $\Delta\tau_d \approx \Delta\tau$ . (vi) The LTADs and TPDDs break the local atomic and electronic material symmetry and stability and generate  $\Delta n^{up}$  upward or/and  $\Delta n^d$  downward electron transitions in the HA neighbourhood during the diffusion event. (vii) The  $\delta n = \Delta n^{up} - \Delta n^d$  electron transitions synchronized with the diffusion events can reduce (or enhance) exponentially the diffusion coefficient  $D$  and the pre-exponential factor  $D_0$ , since the activation energy  $\Delta E$  and entropy  $\delta S$  are proportional to  $\delta n$ . Strong dependences of  $\Delta E, \delta S, D_0$  and  $D$  on  $\delta n$  suggest a SLEF-based electron-related explanation for numerous observed but previously not quite understood experimental facts and some empirical equations in atomic diffusion and related phenomena found in various fields during the last 50 years. In this review we consider applications of the kinetic electron-related theory of diffusion to the following processes: self-diffusion and impurity diffusion in crystalline silicon and mercury cadmium telluride compounds, self-diffusion in undoped and doped germanium, sulfur, phosphorus, bismuth and conventional metals (including transitional metals, such as vanadium and zirconium), self-diffusion in silicon-germanium alloys, defect migration and degradation in semiconductor lasers and light emitting diodes. Effects of high pressure on atomic diffusion are also reviewed. Besides, results of the following previous applications of the kinetic electron-related theory to diffusion-related phenomena are briefly summarized: diffusion-related melting dynamics without and under the influence of high pressure; impurity diffusion in amorph-

ous silicon (a-Si); molecular dynamic simulations of fluorine impurities diffusion in a-Si; metal-induced crystallization and silicon diffusion in amorphous hydrogenated (fluorinated) silicon in the presence and absence of metal contacts; interdiffusion in strained silicon-germanium superlattices of nanometer periods; ion-implantation and thermally-induced interdiffusion in Si/Ge superlattices of nanometer periods; kinetics of diffusion-related structural transformations in  $Ti/Si_{1-x}Ge_x$  systems; novel effects of weak magnetic fields on atomic (defect) diffusion and post-implantation damage in HgCdTe and indium antimonide semiconductors and superconducting ceramics implanted at room temperatures. Agreement between the theory and experimental data was found. The following main results obtained in the aforementioned systems and processes are reviewed and summarized. (i) The Arrhenius-like equation for  $D$  and related rate coefficients are derived from the kinetic consideration. (ii) Kinetic electron-related limitations of the Arrhenius equation are found and corresponding causes of the observed deviations from it are explained (e.g. in Si, V, Zr, etc.). (iii) Large observed variations in  $\Delta E$  (by factors of 1.5 to 5 and higher) caused by changes in experimental conditions are explained. (iv) Extremely large variations in experimental  $D_0$  (by factors of about  $10^3$  to tens of orders of magnitude) found in various materials (e.g. Si, Ge, HgCdTe, S, etc.) are explained. (v) An explanation is given for correlations between the observed variations in  $\Delta E$  and  $D_0$  through the compensation effect (CEF) relation  $\ln D_0 = a \cdot \Delta E + C$ . The coefficients  $a$  and  $C$  are expressed in terms of atomic and electronic material characteristics of nanoscopic diffusion events. (vi) Novel diffusion-melting correlations established earlier for elemental and compound materials are reviewed.  $\Delta E$  and  $D_0$ , as well as coefficients  $a$  and  $C$  in the CEF equation, are expressed in terms of the melting point  $T_m$  and entropy  $\Delta S_m$ , in agreement with observations (e.g. for self-diffusion and impurity diffusion in Si and  $Hg_{0.8}Cd_{0.2}Te$ , etc.). (vii) The origin of the empirical equation  $\Delta E \approx 34T_m$  valid for conventional metals is found and deviations from this equation observed in other materials (e.g. Si, Ge, etc) are explained. (viii) "Abnormally" small activation energies  $\Delta E$  and prefactors  $\tau_0^{-1} D_0^{-1}$  in the equation for the time of gradual degradation in semiconductor lasers and light emitting diodes are explained. (ix) Explanations are given for "normal" ("anomalous") changes of pressure-dependent diffusion coefficient  $D(P)$  in "normal" ("abnormal") materials (e.g. in uranium, etc.). (x) The compensation effect and diffusion-melting correlations established for atomic diffusion in the solid under the influence of steady and time dependent pressure are reviewed. (xi) The conclusion of the SLEF-based kinetic theory about the permanent existence in the solid of the "gas" (or random dynamic arrays) of SLEF-generated simultaneously occurring diffusion events (SODEs) is discussed. The properties of the SODE "gas" and the exponential temperature and pressure dependences of the "gas" cubic density are reviewed. (xii) Effects of high pressure (steady and time dependent) on the SODE "gas" and some related phenomena are discussed. Agreement between the SLEF-based kinetic theory and experimental data is found.