phys. stat. sol. (b) **215**, R1 (1999)
Subject classification: 78.55.Hx; 71.35.Cc; S5.2

Excitonically Induced Defect Annihilation in Solid Krypton

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(Received July 5, 1999; accepted July 16, 1999)

Subthreshold irradiation of solids induces a variety of elementary inelastic atomic processes including defect formation, sputtering, surface and interface reactions [1]. Point defect formation, diffusion and annihilation stimulated by subthreshold excitation of an electronic subsystem of crystals are the subject of active current investigations [2]. In rare gas solids (RGS) the self-trapping of excitons is one of the ways of energy localization and subsequent bond scission [3]. Defect formation induced by electronic transitions (DFIET) was found in RGS at subthreshold excitation by a low energy electron beam [4]. The basis for the DFIET is a concentration of the electronic excitation energy within a volume about that of a unit cell. The energy release can stimulate a displacement of the atom to the defect position in a crystal lattice. In solid Kr the accumulation of stable Frenkel vacancy–interstitial (v–i) pairs is been found to be a result of sample irradiation by subthreshold electrons [5].

On the other hand, in crystals with preirradiated defects the energy release during exciton relaxation may induce a defect transformation or even an annealing. Several microscopic mechanisms have to be considered. In the middle of the excitonic band the free-exciton states are strongly mixed with local-center vibrational states related to the site with excited atom [6] and the generation of highly excited local centers can affect the lattice rearrangement. The self-trapping of excitons is accompanied by the formation of bubbles around the excited centers. Recent molecular dynamics simulations show local heating and lattice oscillations during bubble formation [7] which may induce a lattice instability. The relaxation of the molecular self-trapped excitons by relaxation jumps and an explosion-like emission of phonons [8] induce the lability of the lattice and the preirradiated defects can be annealed.

The cathodoluminescence studies revealed that at non-selective excitation of RGS the relatively weak processes of defect annihilation were hidden by DFIET [5]. The aim of the present study is to separate the defect annealing processes induced by excitons from DFIET using selective photoexcitation of the samples by synchrotron radiation. The experiments were performed at the SUPERLUMI experimental station at HASYLAB, DESY, Hamburg. The crystals of solid Kr were grown from high purity vapor phase in a special cryogenic cell [9] in an UHV environment. The samples were excited by photons with energies $E_{ex} = 10.55$ eV near the middle of the excitonic $\Gamma(3/2)$ $n = 1$ band. Ratner [6] showed that in this energy region the local-center absorption occurs. The luminescence was measured with a 0.5 m-Pouey monochromator ($\Delta\lambda = 25$ Å) equipped with a multisphere-plate detector.

The internal structure of the luminescence bands of self-trapped excitons were used to control the crystal quality of the samples. Radiative decay of molecular trapped excitons in solid Kr produces a so-called M-band. This band is formed by transitions from the $Kr_2^*(^{1,3}\Sigma_u^+;\ 0_u^+,\ 1_u,\ 0_u^-)$ excited states to the ground state $Kr_2(^3\Sigma_g^+;\ 0_g^+)$. The shape of the M-band can be well approximated by two Gaussians: low energy subband M_1 and high energy one M_2 [5]. These subbands with FWHM of 0.44 eV and 0.41 eV are situated at 8.44 eV and 8.64 eV. The subband M_2 is due to the exciton self-trapping in the regular lattice while the component M_1 is due to the trapping at the lattice defects. The dose dependence of these components under irradiation reflects the changes in defect concentration. In the high-quality crystals, DFIET causes an increase of M_1 relative to M_2 with increasing dose [5], and electronically induced defect annihilation is hidden. To reveal the process of annihilation, the concentration of initial defects should be high enough. We have succeeded in detecting the defect annihilation with a sample which was grown by fast condensation at $T = 55$ K and fast cooling to $T = 6$ K. Fig. 1 shows the time evolution of the M-band under irradiation. The intensity of the "defect" M_1-subband decreases with time of irradiation whereas M_2-subband grows in intensity. This redistribution of the intensities between the subbands in

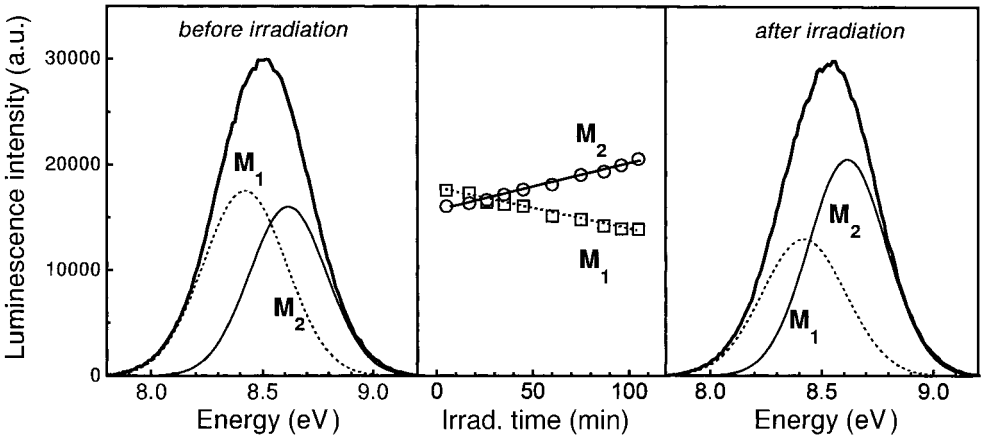

Fig. 1. The evolution of M-band under selective photoexcitation at $T = 6$ K

favour of M_2 reflects the excitonically stimulated defect annihilation. Local heating of the lattice during exciton self-trapping increases the mobility of the Kr interstitials and a recombination of (v–i) pairs occurs. Since the energy of electronic excitation is transferred into a kinetic energy of atomic motion over a unit cell, the annealing of three-, two-, or one-dimensional defects is ruled out. The radiation induced diffusion of interstitials or vacancies results in a defect annihilation at the lattice imperfections such as surfaces, interfaces, dislocations, and voids.

To the best of our knowledge this is the first report on defect annihilation induced by localization of electronic excitation in rare gas solids.

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