Low-temperature desorption of solid argon stimulated by hot excitons

E. V. Savchenko, I. Ya. Fugol', O. N. Grigorashchenko, S. A. Gubin, and A. N. Ogurtsov

B. I. Verkin Physicotechnical Institute of Low Temperatures, Ukrainian Academy of Sciences, Kharkov

Exciton-stimulated desorption of excited argon atoms is studied by using luminescence VUV spectroscopy. The channels of desorption associated with self-trapping of surface excitons and self-trapping of bulk excitons in the surface region of the crystal are analyzed. It is shown that the nonthermalized excitons play the major role in the transport of excitation energy to the surface.

Cryocrystals of all inert elements display the well-known classical mechanisms of thermally stimulated desorption as well as desorption during elastic scattering of high-energy particles by atoms. A new type of desorption stimulated by electron excitations was observed in experiments of diffraction of slow electrons[1] under the conditions in which the above mechanisms are ruled out. This phenomenon has evoked increasing attention and has been studied for various classes of solids.[2,3] Desorption of argon has been investigated upon excitation by ions,[4,5] electrons,[6,7] and photons.[8,9]
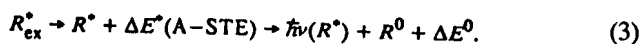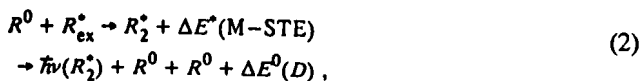
The desorption stimulated by excitations in the electron subsystem consists in the conversion of the electron excitation energy into the kinetic energy of atoms. The necessary condition for such a conversion is the localization of excitations in the surface region, which is accompanied by the liberation of energy in excess of the binding energy ε_b.

When the excitation energy is higher than the forbidden energy gap E_g, charged states, viz., electrons (e) and holes (R_H^+), which can be self-trapped in a regular lattice with the liberation of the energy ΔE^+(STH), are formed in the crystal. Dissociative recombination of self-trapped holes (R_2^+) with electrons, which is accompanied by the liberation of energy ΔE(DRec), may lead to desorption of excited atoms and atoms in the ground state (reaction 1):

$$R^0 + R_H^+ \rightarrow R_2^+ + \Delta E^+(\text{STH}) \rightarrow R_2^+ + e$$
$$\rightarrow R^0 + R^* + \Delta E(\text{DRec}). \tag{1}$$
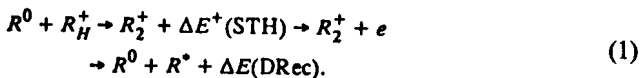
Here R^* is the atom in an excited state and R^0 the atom in the ground state.

The filling of exciton states (R_{ex}^*) followed by self-trapping leads to the formation of states of the molecular (R_2^*) and atomic (R^*) types (the M-STE and A-STE states respectively). Self-trapping is accompanied by the liberation of the energy ΔE^*(M-STE) in the lattice during the formation of a quasi-molecular center and ΔE^*(A-STE) during the formation of a quasiatomic center. The corresponding reactions have the form

$$R^0 + R_{ex}^* \rightarrow R_2^* + \Delta E^*(\text{M-STE})$$
$$\rightarrow \hbar\nu(R_2^*) + R^0 + R^0 + \Delta E^0(D), \tag{2}$$

$$R_{ex}^* \rightarrow R^* + \Delta E^*(\text{A-STE}) \rightarrow \hbar\nu(R^*) + R^0 + \Delta E^0. \tag{3}$$

Here $\hbar\nu(R_2^*)$ and $\hbar\nu(R^*)$ are radiative transitions of the quasimolecular and quasiatomic centers to the ground state. At the

final stage of reaction (2), the centers of the molecular (excimer) type split into two atoms in the ground state. The solution of the dynamic problem[10] shows that in the case of reaction (3) both an excited atom and an atom in the ground state can be desorbed during self-trapping of an exciton at an atom near the surface. It is essential that in reactions (1)-(3) the energy is liberated at the localization stage as well as at the excitation stage. According to reactions (1) and (2), molecules R_2^* can also be the products of desorption.

In most experiments (see, for example, Refs. 4, 6, 8), the total yield of neutral atoms was measured. The partial contribution to the desorption of excited atoms was singled out in Refs. 7 and 9, where it was shown to be directly stimulated by the primary excitation of excitons. It was found that both surface and bulk excitons take part in this process.[9] However, the energy group of excitons which makes the main contribution to the energy transfer to the surface has not been determined so far.

In the present work, we investigate the desorption of excited argon atoms by using the luminescence VUV spectroscopy. The dependence of spectral characteristics on the sample thickness, the energy of exciting electrons, and temperature was measured in the temperature range 5-40 K. The samples were grown from the gaseous phase by condensing on the cooled substrate in a helium cryostat. The degree of dispersion of the samples was determined by varying the condensation conditions, i.e., temperature, pressure, and deposition rate. The samples grown at $T < 0.3 T_t$ (T_t is the temperature corresponding to the triple point) have a finely dispersive structure with a developed surface. Coarse-block condensates were grown at $T > 0.5 T_t$. The energy of exciting electrons was varied between 200 and 2000 eV. In order to eliminate the contribution of the elastic scattering mechanism to desorption, most experiments were carried out in the subthreshold conditions.

Figure 1 shows the luminescence spectra of "thin" ($d < 10$ nm) and bulk ($d \sim 10^3$-10^4 nm) samples of solid argon. The spectra of bulk samples are characterized by the exciton peak[11] E corresponding to the emission from the band $\Gamma(3/2)$, $n = 1$ and radiation bands corresponding to emission from self-trapped states of the A-STE and M-STE type. The A-STE spectrum of the centers consists of the bands a_1, b_2, and c genetically linked with the transitions from the states.[12] $^1P_1$, $^3P_1$, and $^3P_2$ in a free argon atom.[12] Quasimolecular luminescence of bulk centers is presented by the band M corresponding to
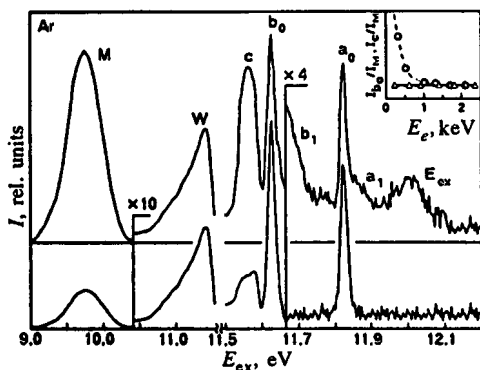
FIG. 1. VUV luminescence spectrum of argon at $T = 5$ K for thin (lower curve) and bulk (upper curve) samples. The inset shows the dependence of the intensity of radiation emitted by a bulk A-STE center (Δ) and a desorbed atom (o) on the energy E_e of exciting electrons. The intensity of the corresponding components c and b_0 is reduced to the intensity of radiation emitted by a bulk M-STE center.

transitions from the states $^{1,3}\Sigma_u^+$. These peculiarities in the spectrum are observed simultaneously in view of the coexistence of different exciton states, viz. free and self-trapped states.[13] This coexistence is ensured by the potential barrier H_{max} separating these states in the bulk of the regular lattice:

$$H(\alpha) = B[\alpha^2 - \Lambda\alpha^3].$$ (4)

Here $H(\alpha)$ is the total energy of the system, B the exciton band halfwidth, α the variation parameter equal to a/r_{loc} (r_{loc} is the localization radius and a the lattice constant), and $\Lambda = E_{LR}/B$ the exciton—phonon interaction constant (E_{LR} is the relaxation energy of the lattice).

In addition to the peaks mentioned above, the spectrum contains the bands W, a_0, and b_0. Their detection and identification[14,15] formed the basis of subsequent investigations of desorption. The W band is formed by transitions from vibrationally excited levels $^3\Sigma_u^+$ in an argon molecule desorbed at the crystal surface.[5] Figure 1 shows that the "0"-components determine the spectra of thin samples. In the case of excitation by slow electrons ($E_e < 1$ keV) with a small penetration depth, these components dominate in the spectrum of bulk samples and disappear if a thin layer of some other gas (Ne or N_2) is deposited on the sample surface. According to Refs. 7 and 12, the "0"-components are characterized by the absence of a matrix shift and a small band halfwidth which does not exceed the spectral halfwidth of the gap. These peculiarities are due to the fact that radiation centers are in the gaseous phase.

However, excited states are populated in the solid phase. Effective mechanisms of dissipation of electron excitation energy lead to a strong redistribution of intensities I in favor of the transition from a lower-lying $^3P_1$ state. These facts receive a natural explanation if we consider the mechanism of exciton-stimulated desorption.[10] Indeed, the excitation of the upper-lying exciton states renders the self-trapping process parallel to relaxation over energy levels. The "memory" of steady-state population density is stored in the intensity distribution between electron transitions in the luminescence spectrum. The radiation process following the ejection of excited atoms occurs in the gaseous phase and is characterized by spectral

parameters typical of a free atom. An atom is ejected under the action of repulsive forces between the excited atom and the atoms of the surrounding lattice due to a negative electron work function for argon.

The desorption is illustrated graphically in Fig. 2 where two dependences are compared, viz., the variation of the intensity ratio of the bulk (M) and surface (b_0) bands on the radiation time t, and the dependence of this ratio on the thickness. A change in the ratio I_M/I_{b_0} during radiation in favor of the surface band points towards a decrease in the sample thickness. Since irradiation is carried out in the subthreshold conditions (by electrons having an energy insufficient for knocking an atom from the sample by a direct impact) at low temperatures, we can state that the observed desorption is stimulated by the excitation of the electron subsystem. It follows from Refs. 7 and 9 that according to reaction (3), the exciton self-trapping is the stimulating factor. It is important that desorption of excited atoms from the surface is developed at the self-localization stage. As in the case of defect formation in the bulk,[16] which follows a similar mechanism, the desorption does not compete with radiative decay.

The exciton-stimulated desorption considered above may serve as a proof of exciton self-trapping in the surface layer of the crystal. The following cases can be singled out:

(1) localization of surface excitations formed at the crystal—vacuum interface, and

(2) localization of bulk excitations arriving at the crystal surface.

Case (1) corresponds to thin samples. The lower curve in Fig. 1 shows that free surface excitons are not detected in radiation, and only the peculiarities associated with self-localization of excitons, viz., radiation lines emitted by desorbing atoms, are observed. The emergence of one of the alternative types of states in the surface luminescence spectrum is in agreement with the peculiarity of the self-trapping model in the two-dimensional case, i.e., the absence of a barrier. In this case, the total energy of the system has the form[17]

$$H_s(\alpha) = B_s\left[\alpha^2 - \Lambda_s\alpha^2\right].$$ (5)

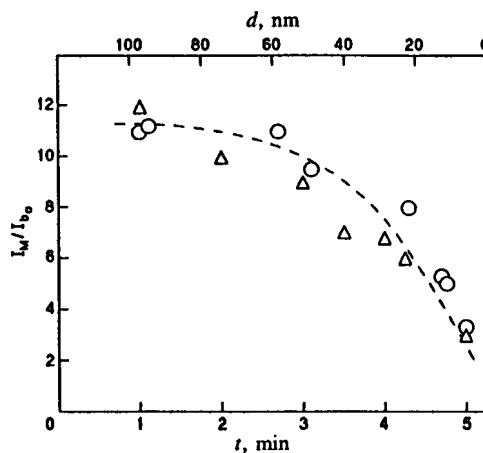**FIG. 2.** Dependence of the relative radiation intensity of bulk centers (band M) and desorbed atoms (band b_0) on the radiation dose (Δ) and sample thickness (o).

The quantities H, B, and Λ with the subscript s correspond to surface states. Depending on the magnitude of the interaction constant $\Lambda_s = E_{LR}{}^s/B_s$, either free or self-trapped states of surface excitons are realized. If $\Lambda_s < 1$, self-trapping does not take place. For $\Lambda_s > 1$, excitons are self-trapped without a barrier. The estimate of the parameter Λ_s of self-trapping at the surface obtained by using the calculated shift of the ground state, the quantities B_s and the Stokes shift gives for argon $\Lambda_s > 1$, which indicates the fulfillment of the self-trapping criterion. In accordance with the barrierless nature of self-trapping, the desorption yield remains constant in the temperature interval where the thermal ejection of atoms does not occur (lower curve in Fig. 3).

Case (2) corresponding to the desorption stimulated by exciton self-trapping near the surface necessitates the stage of energy transport by excitons. The information about transport processes can be gained from the temperature dependence of the desorption yield for bulk samples. The efficiency of desorption is proportional to the number $N(\varepsilon_k, T)$ of excitons participating in the transfer of excitation to the surface and to the diffusion coefficient $D(\varepsilon_k, T)$ for free excitons:

$$I_d \sim N(\varepsilon_k, T) \, D(\varepsilon_k, T),\tag{6}$$

where ε_k is the energy of free excitons with a momentum k. For $\varepsilon_k \gg T$, the exciton distribution function over the band weakly depends on temperature,[18] and hence the temperature dependence of the desorption yield is mainly determined by diffusion of free excitons. The upper curve in Fig. 3 shows the temperature variation of the luminescence intensity of ejected argon atoms. The results obtained for ${}^1P_1$ (o) and ${}^3P_1$ ($\triangle$) states are combined on the curve. The intensities a_0 and b_0 of the components are normalized to their values at $T = 5$ K. The desorption yield of excited atoms in the temperature range 5-14 K remains unchanged. As the temperature increases further to 25 K, the desorption yield decreases nearly in proportion to T^{-1}. A transition to the dependence $I_d \propto T^{-1}$ occurs at a certain "critical" temperature $T_c \simeq 13$ K, whose position is marked by the arrow in Fig. 3. For $T > 25$ K, a considerable contribution to desorption comes from thermally stimulated processes leading to an increase in the desorption yield. The behavior of the upper curve at low temperatures can be explained if we assume that the energy is transferred by

"hot" nonthermalized excitons. According to the theoretical analysis carried out in Ref. 18, the diffusion coefficient D^* of "hot" excitons remains unchanged up to the critical temperature T_c. Above T_c, the diffusion coefficients $D^*(T) \propto T^{-1}$. A change in the form of the dependence $D^*(\varepsilon_k, T)$ occurs at

$$T_c \sim 2\hbar ks = 2\left(2ms^2\varepsilon_k\right)^{1/2},\tag{7}$$

where s is the velocity of sound and m the exciton mass. The value of the critical temperature was estimated by taking into account the fact that the exciton distribution has a peak in the region of H_{max}, viz., the top of the self-trapping barrier.[19] The most intense transition of excitons to the self-trapped state occurs before their thermalization near H_{max}. As a result, the number of excitons having energies $\varepsilon_k < H_{max}$ decreases considerably, and the main contribution to the transfer must come from "hot" excitons with energies $\varepsilon_k > H_{max}$. The estimate based on formula (7) for $\varepsilon_k = H_{max}$ by using the values of H_{max} presented in Ref. 13 gives $T_c \simeq 13$ K for argon. The value of T_c obtained in the present work is in good agreement with the theoretical estimate obtained in Ref. 18. The temperature dependence of the desorption yield measured by us correlates with the temperature dependence of luminescence of impurities in the argon matrix, caused by the participation of "hot" excitons in the excitation energy transfer to the impurity centers.[18] It should be noted that the characteristic temperature dependence of desorption is observed during self-trapping of triplet $\Gamma(3/2)$ as well as singlet $\Gamma(1/2)$ excitons in the A-STE states.

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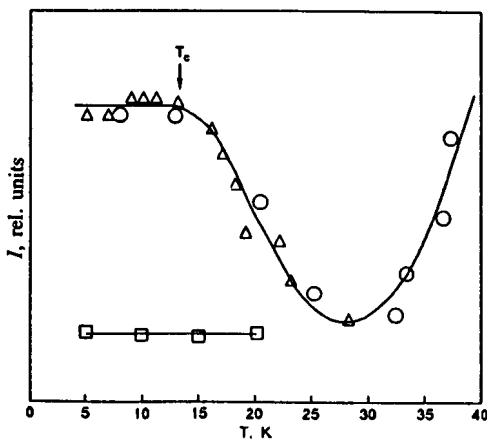
FIG. 3. Temperature dependence of the radiation intensity of desorbed atoms for a thin (lower curve) and bulk (upper curve) sample.

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