Penetration Depths of Photomobilized F Atoms from a Sandwich Experiment

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A long range migration with a mean penetration depth of 2.8 nm was determined for photomobilized F atoms with kinetic energies of 4.2 eV in an Ar film. Migration in a sandwich with F atoms generated by F_2 photodissociation in a top layer, transport through the Ar spacer layer with variable thickness, and efficient detection by Kr exciton enhanced Kr_2F fluorescence on an Ar/Kr interface was applied for the first time as a direct and reliable measurement of the distribution and mean value of the penetration depth.

Photomobility is based on electric excitation of a particle in a crystal which gains kinetic energy by a structural rearrangement in an excited or in the final ground electronic state. The distance between the original lattice site of the hot atom and the position where it comes to rest again due to dissipation of its kinetic energy corresponds to its penetration depth, and this penetration depth is a characteristic property for the photomobility. Transport of energy and electrons in a crystal after excitation by light or particles has been investigated extensively by using layered systems. Studies of the penetration depth of photomobilized particles within the crystal are quite scarce because most experimental investigations deal with desorbed and sputtered particles or with the stopping power of particles which are accelerated into the sample [1]. On the other hand, this penetration depth is a very relevant quantity, for example, for light induced damage, color center formation, and solid state photochemistry. A direct and reliable novel technique is therefore presented in this contribution for the determination of the mean range of photomobilized atoms. Elementary photochemical processes and especially the cage effect have been treated experimentally [2,3] and theoretically [4,5] using rare gas films doped with small molecules as prototype systems within the last years. An appropriate way to investigate the photomobility in such systems involves photodissociation of a diatomic molecule on a repulsive surface in a rare gas matrix and determination of the range of the fragments. In this context is should be mentioned that the thermally induced diffusion of fragments was investigated by some groups, i.e., for H atoms [6,7], but this process is not our topic. We focus on the penetration depth of the fragments due to the initial kinetic energy acquired in the dissociation process. In this spirit the penetration depth was estimated previously for F atoms with few eV kinetic energy from the balance of geminate recombination and recombination of fragments from different sites [8] or from the competition of geminate recombination and recombination with an acceptor which is additionally doped in the matrix [9]. These methods require assumptions on the statistical distributions of the dopants which are diffi-

cult to justify, and they suffer from the averaging over the statistical separations.
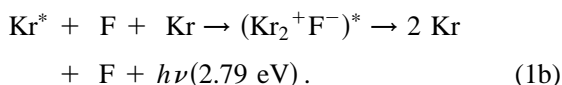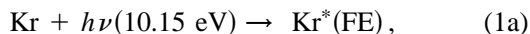
These deficiencies are avoided in the technique presented here which uses a sandwich of three films with thicknesses in the monolayer regime. The top rare gas film Rg is doped with the diatomic, the intermediate film is a pure rare gas of the same or a different kind Rg′, and the third film is used for detection and consists of another rare gas Rg″. A fragment X is generated with excess energy by photodissociation of the diatomic in Rg; it can enter Rg′ and eventually cross this intermediate film, finally reaching the detection layer Rg″. Since the spectroscopic properties of X, like fluorescence band energies, will be different in general in Rg′ and Rg″, it is possible to detect the arrival of the atom X at the detection layer surface. In this case the migration across the intermediate film with thickness d can be monitored directly. The intensity of fluorescence from XRg″ versus d yields the probability for a crossing of Rg′ and thus the mean penetration depth l of the fragment and its distribution. Since l values in the order of only a few lattice constants, i.e., some monolayers (ML) can be expected, it is crucial to prepare smooth films with a stepwise change of composition and with controlled thicknesses.

The selection of the specific system, namely, to measure the penetration depth of F atoms in Ar matrices from dissociation of F_2, results from two reasons: In a previous study in mixed F_2/Kr/Ar systems rather large l values of about 25 ML [9] were estimated. Furthermore, molecular dynamics calculations were carried out for the F_2/Ar system with contradictory results. One supports the large experimental value [10], and the other one predicts no photomobility for small kinetic energies [11].

The experiments were performed at the 3mNIM2 beam line at the electron storage ring BESSY I in Berlin, which provides tunable radiation in the wavelength range from 50 to 300 nm with an intensity of more than 10^{15} photons/cm^2s within a typical bandwidth of 0.2 nm in a focal spot with a size of 0.2×0.5 mm^2 on the sample. A commercial quartz microbalance is mounted next to the MgF$_2$ substrate, and both are thermally

connected by the cooling finger which is cooled by a liquid He flow cryostat down to 4 K. The pure rare gases Kr and Ar and the Ar/F_2 gas mixture (two concentrations 0.5% and 2%) were condensed one by one with a continuous flow from three independent gas deposition tubes. The deposition rates were adjusted by sensitive needle valves for each gas to about 0.1 nm/s. This setup with the three different reservoirs and tubings avoids interdiffusion between the different films and suppresses the possibility of gas mixing prior to and during condensation. The microbalance was calibrated individually for each deposition tube by comparison with oscillations in the reflectivity of the films at 150 nm wavelength due to interference effects. The resolution for the frequency reading of 1 Hz leads to an accuracy for the film thickness of better than 0.2 nm.

In general the sandwiches were composed of 30 nm Kr, 5 nm Ar/F_2 (with an F_2 concentration of 0.5%), and an intermediate Ar film with a thickness in the range between 0 and 20 nm. The growing sandwich was irradiated during deposition with monochromatic synchrotron radiation of $h\nu = 10.15$ eV, which corresponds to the energy of the first ($n = 1$) Kr^* exciton [12]. In preliminary experiments we confirmed that this energy (i) dissociates F_2 molecules doped in Ar matrices efficiently, (ii) there is no strong absorption in this energy region leading to Ar_2F fluorescence, and (iii) excited Kr excitons can efficiently transfer energy [12] on the Kr/Ar interface to the trapped F atoms resulting in their characteristic Kr_2F fluorescence,

$$Kr + h\nu(10.15 \text{ eV}) \rightarrow Kr^*(FE), \quad (1a)$$

$$Kr^* + F + Kr \rightarrow (Kr_2{}^+F^-)^* \rightarrow 2\,Kr$$
$$+ F + h\nu(2.79 \text{ eV}). \quad (1b)$$

Condition (ii) indicates that F atoms in Ar cannot be excited, and therefore an increased photomobility due to successive excitation of Ar_2F in the intermediate Ar layer releasing mobile F atoms after radiative relaxation [8] can be excluded. Condition (iii) is very supportive, since the signal is not limited by the rather low absorption of the diluted atoms on the Kr surface and the strong absorption in the ($n = 1$) Kr exciton [13] is exploited to obtain a large fluorescence signal. The characteristic Kr_2F fluorescence is centered around 439 nm within Ar matrices and around 453 nm in Kr matrices [9]. The fluorescence of Kr_2F in the sandwich is centered around 444 nm just in between the values for pure Ar and pure Kr. This illustrates that the detected F atoms in the sandwich are located right at the Kr-Ar interface. When irradiating the growing Kr and Ar films, a slow increase in the background fluorescence in general and also at the fluorescence wavelength of 444 nm is observed. This background can be well separated from the steep increase at 444 nm after condensation of the Ar/F_2 mixture (Fig. 1). The growth curve with Ar/F_2 is due to photodissociation of F_2 and successive migration of the

hot F atoms through the intermediate Ar film to the Kr substrate where they are trapped and subsequently excited via energy transfer from Kr^* ($n = 1$) excitons. According to previous studies [9] and recent calculations [14], there is no significant photomobility expected for the F atom fragments after radiative relaxation of electronically excited Kr_2F to the repulsive ground state surface because the excess kinetic energy is released mainly along the Kr-Kr coordinate, and therefore the F atom gains very little kinetic energy. This picture is in accord with our growth curve showing a saturation plateau of the Kr_2F intensity indicating the stabilized sites of the F atoms at the Kr-Ar interface. For Kr_2F initiated mobility a decrease due to F atoms migrating back into the interstitial Ar layer would be expected. The saturation intensity (after subtraction of the background) of one prepared sandwich yields for the chosen Ar spacer thickness one point in the plot in Fig. 2. After compilation of the results for 22 sandwiches we obtain a decrease of the saturation intensities with d which is quite well described by an exponential (dotted curve in Fig. 2) with a mean value for the range of 2.8 nm. Of course the smoothness of the sandwich is critical since holes in the film would lead to an overestimation of the range. The complete coverage was checked via the surface excitons of the Kr substrate which disappear for a covered surface [12,15]. Closed films were obtained for deposition rates below 0.2 nm/s. Migration experiments were performed only for samples with quenched surface excitons.

Some remarks are in order with respect to the F_2 dissociation. F_2 will be predominantly dissociated by direct photoabsorption, but especially for thin Ar spacer layers a contribution by a Förster-Dexter type [16] energy transfer from the Kr excitons is possible [17]. The superposition of both processes would be evident in the dose dependence of the growth of the Kr_2F signal in Fig. 1 and an energy transfer contribution would result in an increased early rate. For the determination of
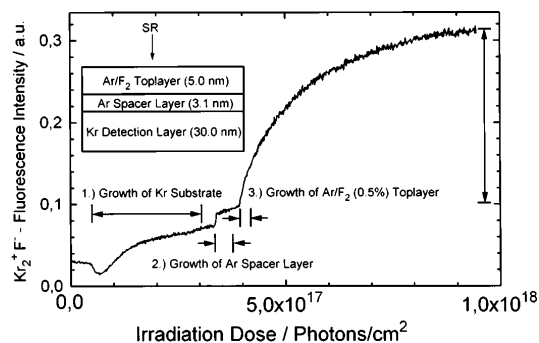

FIG. 1. Intensity dependence of Kr_2F fluorescence at 444 nm for irradiation with 10.15 eV during sandwich condensation (1, 2, 3) indicating a background (0.1 a.u.) and a growth by a factor of 3 of the relevant signal to a saturation value after completing the Ar/F_2 top layer. Thicknesses of Ar spacer, top layer, and detection layer were 3.1, 5, and 30 nm, respectively.
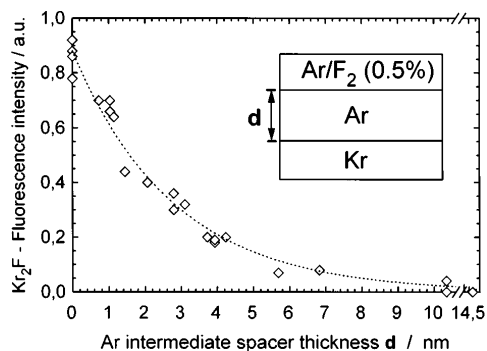
FIG. 2. Collection of the saturation intensities of Kr_2F fluorescence (Fig. 1) of 22 samples with Ar spacer layer thicknesses between 0 and 14.5 nm for an F_2 concentration of 0.5% representing the distribution of penetration depths of the photomobilized F atoms through the spacer layer. Dashed curve: exponential fit with a mean penetration depth of 2.8 nm. Top and detection layer thicknesses as in Fig. 2.

the range in Fig. 2 a separation of these contributions is not necessary because these values are taken from the saturation intensity for large doses corresponding to maximal achievable dissociation.

The excitation energy provided either by direct photoabsorption or by energy transfer of about 10 eV is too small to reach the lowest bound Rydberg or charge transfer states of F_2 according to gas phase potential surfaces [18] and the spectroscopy in Ne matrices [19]. A broad absorption band is observed in Ar around 10 eV which is in accordance with the vertical transition energies of several repulsive F_2 states [18] and a similar absorption band between 9.7 and 11 eV shows up for F_2 in Ne. Thus a kinetic energy of about 8.5 eV is available for the two F atoms when the binding energy is included, and each F atom will be prepared with about 4.2 eV kinetic energy for a symmetric distribution.

F atoms with this kinetic energy have a mean penetration depth of 2.8 nm according to Fig. 2 and the penetration depths of the individual atoms are distributed exponentially. In the molecular dynamics simulation of Ref. [10] a predominant symmetric exit for F_2 dissociation in Ar was derived and for the highest kinetic energies of 1 and 1.4 eV one and four long range trajectories ($l > 1$ nm) out of 50 were obtained, respectively. Characteristic for all long range trajectories was a wiggly motion along a lattice diagonal, i.e., along a channel in the lattice, without side steps. These predictions are in qualitative agreement with our results. Nevertheless, the size of the clusters and the statistics have to be improved considerably together with an extension to higher excess energies for a quantitative comparison. Extensive diatomics in molecules calculations were carried out to derive the potential surfaces in the molecular dynamics calculations of Ref. [11], and a full cycle consisting of an excitation of an ArF exciplex and its radiative decay was simulated.

Only one trajectory consisting in a jump to the next interstitial lattice site out of 100 showed photomobility at all with kinetic energies of 0.07 to 0.12 eV acquired on the ground state surface. Obviously the kinetic energies reached by the Ar-F interaction are too small.

Long range mobility with a mean range of 7.0 nm was derived experimentally from the second order rate constant for photomobility induced recombination initiated by Ar_2F decay [8]. This is just process analyzed in Ref. [11], and the quantitative values should be reexamined in view of the small kinetic energies involved. In Ref. [9] it was demonstrated that photomobilized F atoms migrate in multiply doped matrices from one rare gas trap to another, and from the concentration dependence a mean penetration depth of about 3.0 nm was estimated. This result is in qualitative agreement with the penetration depths anticipated from the high densities of XeF centers in Ar matrices which are required for laser operation [20]. These methods can be used as a qualitative guide to search for systems with a potentially long penetration depth and then the sandwich technique has to be applied to derive the range distributions and reliable mean values.

Future extensions with respect to the F transport problem including tuning of the dissociation wavelength to very the kinetic energy, exchange of the spacer layer by other rare gases, modification of temperature and degree of disorder in the spacer layer, and the use of nonsymmetric parent molecules are quite obvious. Different classes of atoms can be studied and the ranges of H and D atoms seem to be especially interesting [6,7]. Finally reaction partners can be introduced at the surface of the detection layer and the reaction products can be detected with high efficiency by exploiting the energy transfer by excitons from the detection layer according to our results. A large collection of prototype photoreactions has already been studied by matrix isolation spectroscopy in the conventional multiply doped way [21]. The different steps in photochemistry consisting of (i) the cage exit of the reactive fragments, (ii) transport of the fragments, and (iii) reaction to a new compound can now be studied separately in the solid phase in such sandwich systems with respect to a theoretical treatment.

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