EXOELECTRON EMISSION FROM THIN FILMS OF ALKALI METAL HALIDES

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Photostimulated emission of electrons from thin films of NaCl, KCl, KBr and KJ excited by irradiation with X-rays is studied. The films have been deposited by means of the vacuum evaporation method at various deposition rates. The influence of the deposition rate and the intensity of stimulating light on the initial intensity of emission as well as on emission decay rate have been investigated. The existence of a maximum value of the decay constant at a certain deposition rate has been found in case of NaCl and KCl films. The dependence of the initial intensity of emission on the deposition rate also exhibits a disturbance of the monotone behaviour at this particular deposition rate.

Introduction

The study of exoelectron emission is a valuable method of investigating the energy structure of matter and of the analysis of crystal lattice defects. The first applications of this method to the study of alkali metal halide crystals are described in the papers of Sujak (1953, 1956, 1957), Bohun (1955) and other authors.

The analysis of the spectral distribution of the intensity of emission stimulated with light permitted this phenomenon to be connected with the existence of colour centres in ionic crystals. Later authors (*e.g.* Belkind and Nagli (1964)) have pointed out the complex nature of exoelectron emission and the existence of recombination processes.

The exoelectron emission has been also applied to investigations in thin film physics which recently became a new rapidly developing discipline. To obtain by vacuum evaporation thin films with reproducible physical properties is a rather complicated technological problem and therefore information about the structure of such films is particularly useful.

The application of the method of photostimulated emission of electrons to the studies of very thin NaCl-films can be found among others in the paper of Lewowski (1968). The appreciable spread of results found in the latter work is probably connected with the fact that the rate of deposition of the films was not controlled. The results of the present paper

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enable us to conclude that the influence of deposition rate on the emission properties of thin films and thus also on their structure is quite appreciable.

In the investigations made so far it was found that the deposition rate of metal films obtained by vacuum evaporation influences the grain size and the crystal structure of the films (Sennet and Scott, 1950). Cocquet (1967) has found, though only qualitatively, that the deposition rate of thin gold films influences the quantum yield of photoemission. Quantitative measurements of the dependence of quantum yield of photoemission on the deposition rate of Al films will be given in the paper of Lewowski and Pahin (to be published)

Apparatus and method of measurement

The vacuum evaporation process as well as the excitation of the films and the measurement of emission were carried out in the same evacuated vessel (Fig. 1) under the pressure of 10^{-5} Tr without contact with air between the particular operations. The substrates for

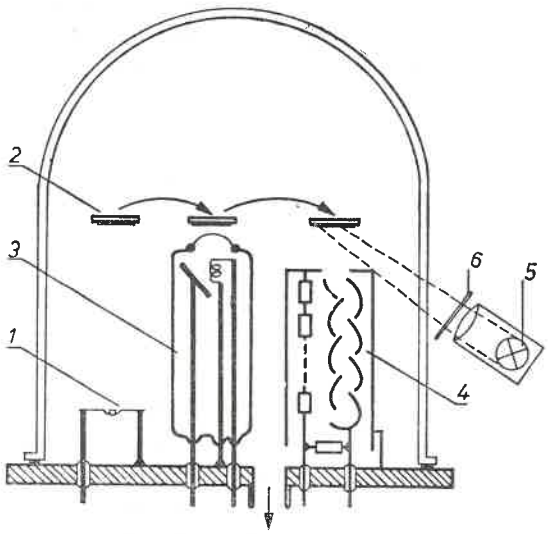

Fig. 1. Schematic drawing of the apparatus

all these films were a nickel foils. The crystal was located in a molybdenium holder *1*. The temperature of the crystal and thus the deposition rate was controlled by controlling the current flowing through the holder. The deposition rate and the film thickness were measured by means of an electronic quartz micro-balance. In order to obtain repeatable results the thickess of the deposited films were the same equal to 100 nm. For this thickness the intensity of exoelectron emission from NaCl samples is already sufficiently high and its dependence on thickness is already negligible (Lewowski 1968).

After the deposition of the film the sample (*2*) was transported in vacuum to the window of an *X*-ray tube *3*, for producing colour centres by irradiating the sample, however, without the access of light. Each sample was irradiated for 10 seconds, the voltage amounting to

10 kV, and the current flowing through the lamp 9 mA. The X-ray tube had a copper anode and a lithium glass window with a thin aluminium film deposited on it which transmitted soft X-rays and absorbed light.

After irradiation the sample was transported above the electron multiplier *4*. The latter operated in pulse system. The multiplier was used as detector of the emitted electrons. The number of electrons emitted in unit time was recorded on a paper tape recorder working with standard electronic equipment used in measurements of nuclear radiation.

The stimulating light source was a 20 W tungsten bulb (*5*) located outside the glass vessel. The intensity of incident light was changed by using grey filters (*6*) obtained by means of the photographic method and calibrated by means of vacuum thermo-couple.

Results of measurements

I. Influence of deposition rate

Typical decay curves of exoelectron emission stimulated with white light can be approximated by the sum of several exponential curves (Lewowska and Sujak 1965). Since the decisive influence on the character of the decay curve is exerted by the first component, the present work was concerned with the dependence of the initial value of the emission intensity I_0 (registered at the instant of switching on the stimulating light) and the decay constant λ of the first component on the deposition rate of the emitting film.

It was found that films deposited at a high rate (several nm/s) are characterized by emission with a high initial intensity I_0 and a slow decay. For smaller deposition rates the intensity of emission is smaller and the decay rate increases.

Figs 2, 3 and 4 show the dependence of the initial intensity I_0 and the decay constant λ on the deposition rate v of the particular films. For the NaCl and KCl films a maximum of the decay constant has been observed at small deposition rates (about 0.2 nm/s), this maximum being shifted in case of KCl towards greater deposition rates. A very rapid decay of emission intensity from KBr and KJ films did not permit the study of the character of the decay in case of small deposition rates.

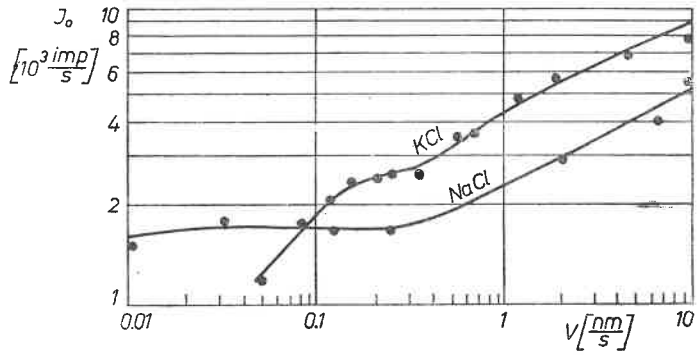

Fig. 2. Initial intensity of photostimulated exoelectron emission from NaCl and KCl films *versus* the deposition rate of films

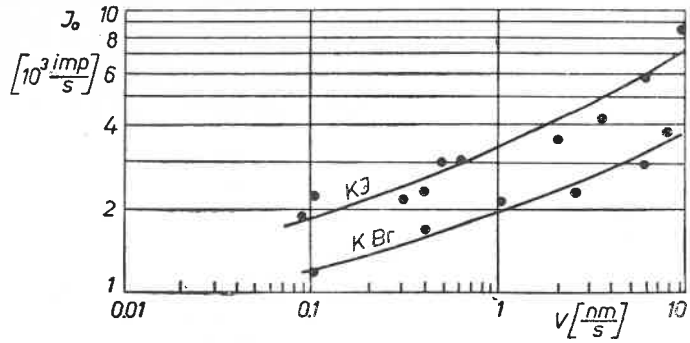

Fig. 3. Initial intensity of photostimulated exoelectron emission from KBr and KJ films *versus* the deposition rate of the films

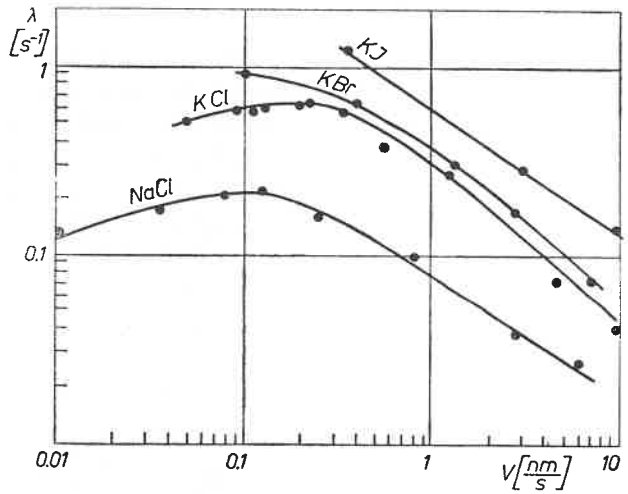

Fig. 4. Dependence of the decay constant of the first component of the photostimulated exoelectron emission intensity curves on the deposition rate for NaCl, KCl, KBr and KJ films

II. Influence of the intensity of stimulating light

The contribution of the particular components to the behaviour of the decay curves is shown in Fig. 5. For high values of the intensity of light (curve B_1) the initial value of exoelectron emission intensity is high and the emission decay is rapid. The dominant role in the emission decay process is played by the first component. At smaller light intensity values (curve B_2) both the intensity of emission and the decay rate are smaller while the contributions of remaining components become greater. When the intensity of stimulating light is further decreased (curve B_3) one can observe a still greater decrease in the initial emission intensity as well as a further decrease in the decay rate. This curve can again be quite well approximated by a single exponential curve.

For very small intensities of stimulating light (B_4) the initial parts of the exoelectron emission curves are first increasing (in case when the deposition rates of the films were

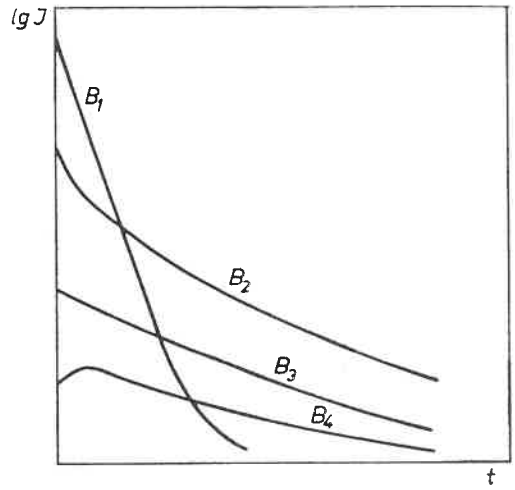

Fig. 5. Typical decay curves of photostimulated exoelectron emission from thin films of alkali metal halides obtained at various intensities of stimulating light. B_1 — greatest intensity of stimulating light; B_2, B_3 and B_4 successively decreasing intensity values

high). However, after a dozen or more seconds the emission intensity becomes maximum and then slowly decreases.

The dependences of the initial emission intensity I_0 and the decay constant of the first component of the decay curve on the intensity of stimulating light are shown in Figs 6

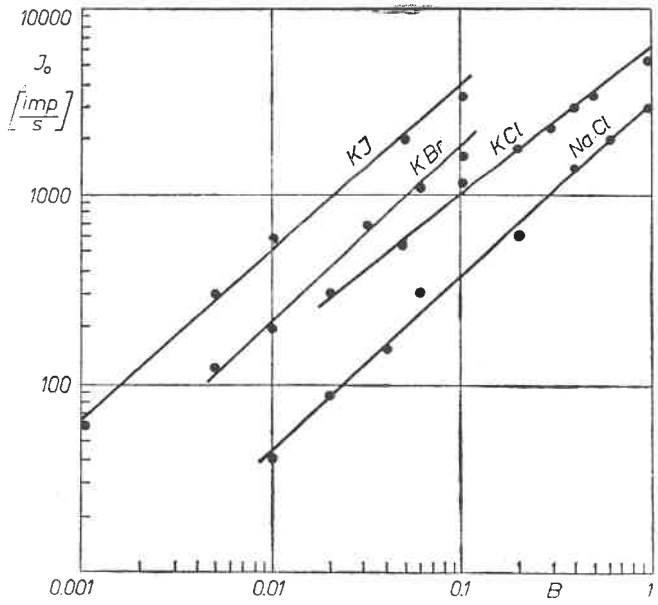

Fig. 6. Initial intensity of photostimulating exoelectron emission from NaCl, KCl, KBr and KJ films as a function of the intensity of stimulating light

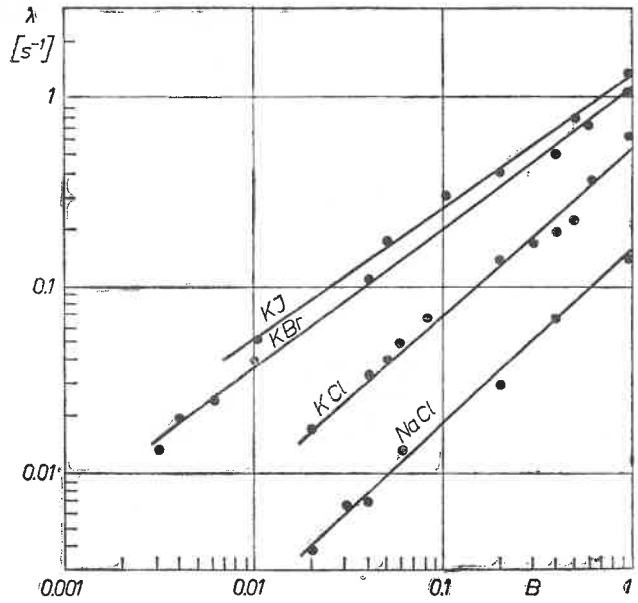

Fig. 7. The decay constant of the first component of the photostimulating exoelectron emission curve as a function of the intensity of stimulating light for NaCl, KCl, KBr and KJ films

and 7, respectively (the intensity of stimulating light B is plotted in relative units). These dependences can be approximated by a power law with exponents of the order of unity. For the same values of the intensity of light the KJ films are characterized by greatest initial exoelectron emission intensity and greatest decay rate. For KBr, KCl and NaCl films the values of initial emission intensity and decay rate become smaller, respectively.

Discussion of results

One can assume that the changes in the intensity and the decay rate of exoelectron emission from thin films of alkali metal halides obtained by vacuum evaporation, observed as a function of time are caused by changes in the crystal structure of these films, similarly as in metal films (Sennet and Scott 1950).

For small deposition rates the deposited films are characterized by a small number of defects with the same values of emission work. For high deposition rates the number of defects is much greater (higher I_0 values) and the spectra of electrons have a more complex character (the appearance of several components in the decay curves).

On can also assume that the electrons are emitted outside from the conduction band and not directly from the defects. In such a case the electrons would be transported by light from colour centres to the conduction band and from there they would be emitted by thermal emission process. In given measurement conditions the number of electrons in the conduction band is proportional to the number of defects.

If the number of free electrons in unit volume of the crystal is denoted by n then

$$n = N_c \exp\left(-\frac{E_{fn}}{kT}\right)$$

where N_c is the density of states in the conduction band while E_{fn} the energy gap between the Fermi quasi level and the bottom of the conduction band. It follows that for a high number of electrons in the conduction band their emission work is smaller than in case when this number is small. The above-mentioned hypothesis of a Fermi quasi level has been proposed by Lewowska and Sujak (1965) in case of Al_2O_3 films in order to explain the influence of the intensity of stimulating light on the shape of the curves of the exoelectron emission decay. It seems probable that in case of films of alkali metal halides the emission mechanism is similar since the character of the time dependence of emission intensity and the dependence of emission intensity on the intensity of stimulating light is in both cases the same.

The above-mentioned effect of emission intensity increase for low intensities of stimulating light has been observed already earlier by Belkind (1962). Itoh and Suita (1962) have suggested that this effect is connected with the high density of colour centres. The latter point of view is confirmed by the present results since the increase in emission intensity as a function of time is characteristic for films obtained by vacuum evaporation with high deposition rates, when the density of defects is high.

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