INSTALAÇÃO EXPERIMENTAL PARA PESQUISA DA EXCITAÇÃO LUMINESCENTE DO FÓSFORO, ESTIMULAÇÃO E EXTINÇÃO POR FEIXES ATÔMICOS E MOLECULARES

EXPERIMENTAL INSTALLATION FOR RESEARCH OF PHOSPHORS LUMINESCENCE EXCITATION, STIMULATION AND EXTINGUISHING BY ATOMIC AND MOLECULAR BEAMS

ЭКСПЕРИМЕНТАЛЬНАЯ УСТАНОВКА ДЛЯ ИССЛЕДОВАНИЯ ВОЗБУЖДЕНИЯ, СТИМУЛЯЦИИ И ТУШЕНИЯ ЛЮМИНЕСЦЕНЦИИ ФОСФОРОВ В АТОМНО – МОЛЕКУЛЯРНЫХ ПУЧКАХ

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Received 26 August 2018; received in revised form 30 November 2018; accepted 31 December 2018

RESUMO

As tecnologias de plasma a gás estão se tornando cada vez mais importantes em escala industrial. Contribuem para a produção e processamento de materiais utilizando o aquecimento dos produtos iniciais no jato de plasma ou a sua transferência para o estado de plasma. Portanto, o objetivo principal do trabalho é estudar a eficiência de um arranjo experimental para estudar a excitação da estimulação e a têmpera da luminescência do fósforo em feixes moleculares atômicos. Para atingir esse objetivo, foi analisada a dissociação de gases em uma descarga indutiva de alta frequência nos principais circuitos de geradores modernizados. O artigo apresenta o projeto, a construção, o hardware da instalação para o estudo da excitação, têmpera e estimulação dos cristais de fósforo por vários métodos quando expostos à superfície de feixes únicos ou cruzados de moléculas de gás e átomos de energia térmica. Fragmentos da cinética e do espectro de fotoluminescência do óxido de ítrio dopado com európio no feixe de átomos de oxigênio foram estabelecidos.

Palavras-chave: fluxos moleculares, separação catalítica, dissociação gasosa, instalação de alto vácuo.

ABSTRACT

Gas plasma technologies are becoming increasingly important on an industrial scale. They contribute to the production and processing of materials using the heating of the initial products in the plasma jet or their transfer to the plasma state. Therefore, the main goal of the work is to study the efficiency of an experimental setup for studying the excitation of stimulation and quenching of phosphorus luminescence in atomic-molecular beams. To achieve this goal, we analyzed the dissociation of gases in a high-frequency inductive discharge in the main circuits of modernized generators. The article presents the design, construction, hardware of the installation for the study of excitation, quenching and stimulation of the crystal phosphors by various methods when exposed to their surface single or crossed beams of gas molecules and atoms of thermal energy. Fragments of the kinetics and photoluminescence spectrum of yttrium oxide doped with europium in the beam of oxygen atoms were established.

Keywords: *molecular flows, catalytic separation, gas dissociation, high vacuum installation.*

АННОТАЦИЯ

Газоплазменные технологии приобретают все большую значимость в промышленных масштабах. Они способствуют получению и обработки материалов с использованием нагрева исходных продуктов в плазменной струе или их перевода в плазменное состояние. Поэтому основная цель работы заключается в изучении эффективности экспериментальной установки для исследования возбуждения стимуляции и тушения люминесценции фосфоров в атомно-молекулярных пучках. Для достижения поставленной цели в работе проанализирована диссоциация газов в высокочастотном индуктивном разряде в основных контурах модернизированных генераторов. В работе представлена схема, конструкционное исполнение, аппаратное обеспечение установки для исследования различными методами процессов возбуждения, тушения и стимуляции люминесценции кристаллофосфоров при воздействии на их поверхность одиночных или скрещенных пучков газовых молекул и атомов тепловых энергий. Установлены фрагменты кинетики и спектра фотолюминесценции оксида иттрия, допированного европием, в пучке атомов кислорода.

Keywords: *молекулярные потоки, каталитическая сепарация, диссоциация газов, высоковакуумная установка.*

INTRODUCTION

Atomic and molecular particles of thermal energy (H, O, N, O₂, CO, SO, etc.) actively influence the processes of excitation, stimulation, and quenching of the luminescence of crystal phosphors through the surface (Volkenshtein *et al.*, 1976; Sancier *et al.*, 1962; Rufov *et al.*, 1996; Breysse *et al.*, 1978; Coon, 1979; Styrov *et al.*, 1989; Denisov *et al.*, 1992; Shigalugov *et al.*, 2000; Styrov *et al.*, 2000; Georgobiani *et al.*, 2002; Shigalugov and Tyurin, 2005; Shigalugov *et al.*, 1996). This influence is of particular importance in connection with the introduction of gas-plasma technologies on an industrial scale (gas-discharge indicators, plasma panels) and the increasing use of nanotubular crystalline materials in modern means of displaying information (Ruchin, 2018). Therefore, a systematic study of these processes, obtaining on this basis new data on atomic-molecular and electronic phenomena in areas adjacent to the boundary between a non-equilibrium gas and a dispersed solid, is an important task of radiation physics, plasma chemistry, nanoelectronics.

For the experiments, we designed, built and put into operation a special high-vacuum ("oil-free" vacuum $\sim 10^{-6}$ Pa) installation using single or crossed beams of gas atoms and heat energy molecules.

The installation (the diagram is shown in the figure 1) includes the following main parts: a vacuum chamber 1 with quartz optical windows 2–5; substrate – microburner 6 with test sample

7, connected to devices for monitoring 8 and adjusting 9 its temperature; replaceable detector 10 of an automatic microcalorimeter 11 for measuring the heat of heterogeneous reactions or the concentration of gas atoms; nozzles 12,13 for forming sample 7 and (or) detector 10 streams (beams) of neutral gas particles along two separate channels; a system for generating gas atoms 14–22; photoexcitation system 23–25 of the sample; lighting and spectral equipment 26–31; pumping means and vacuum fittings 32–41; storage system and preparation of mixtures of pure gases 42, 43; personal computer 44 with peripheral devices 8, 11, 24, 26, 29, 30, 31, 45.46 for the collection, preprocessing and visualization of experimental data.

Used high-purity gases: O₂ (99.999%), H₂ (99.998%), N₂ (99.998%), CO₂ (99.998%), SO₂ (99.9%), CO (99.9%), N₂O (99.9%) are supplied to the needle guides 34,41 through cylinders 42,43 of low ($\sim 10^5$ Pa) pressure through two independent channels. Separate pumping and adjustment of gas pressures to working $1\cdot 10^{-1}$ Pa in fore vacuum lines is carried out by two rotary 35, 40 (Alcatel 2015-5 l s⁻¹) pumps through a system of 36, 39 cooled water and liquid nitrogen nitrogen 37, 38 traps.

MATERIALS AND METHODS

Gas dissociation is carried out in a high-frequency inductive discharge in the main circuits of the upgraded UHF generators – 66 (the frequency on the main harmonic is 40.68 MHz,

the power in the discharge is up to 200 W) 15 and 21. Single and crossed at sample 7 atomized or molecular flows (effusion beams) with an intensity of up to $10^{16} - 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$ are formed in glass discharge tubes 14, 22 with an internal diameter of 29 mm, using conical nozzles 12, 13 holes 0.8 mm. The ends of the nozzles are removed from the surface of the sample at distances of $\sim 30 \text{ mm}$.

From ionized particles and electronically excited oxygen molecules O_2^e ($a^1\Delta_g$, $b^1\Sigma_g^+$ and etc.) disposed of by magnetic 24, 25 and catalytic 17 (layer Co_3O_4 on the part of the inner surface of the "oxygen" discharge tube 14) separation (Ryskin, 1984; Balandin *et al.*, 1999). Wood's light traps 18,19 allow you to suppress the scattered light discharges.

Inert gases Ar (99.998%) or Xe (99.999%) are used to "flush" vacuum lines, ion cleaning the walls of discharge tubes and nozzles. High vacuum up to 10^{-6} Pa in chamber 1 is provided by two magnetic discharge pumps and 32.33 (HMD – 04–400 l / s, HMD-016-150 l / s). In the presence of beams, the dynamic vacuum in the chamber is 10^{-3} - 10^{-4} Pa .

The concentration of oxygen atoms is measured by the method of an isothermal calorimeter (Elias *et al.*, 1959): according to the heat of the recombination process on a replaceable wire detector 10, and in complex gas mixtures – by the luminescence method developed in our laboratory (Shigalugov *et al.*, 1996).

RESULTS AND DISCUSSION:

The concentration of hydrogen atoms is determined calorimetrically, by the method of (Volkenshtein *et al.*, 1976). The fine sample 7 under study is deposited from a suspension on a substrate micro-furnace 6, made according to the type of indirectly heated cathode (profiled nickel substrate protected by a thin layer of SiO_2 with an indirect nichrome heater). A platinum (Pt) thermometer with a multimeter output 8 (B7-21A) is built into the substrate to measure the resistance in a 4-wire circuit. Data from the digital output of the multimeter 8 in a binary-decimal code is transmitted to a personal computer (PC) 44 through the first port of the digital I / O card LA-48D using the interrupt signal generated by B7-21A. The resistance values of the Pt-thermometer obtained from the multimeter are

converted to temperature values according to a predetermined tabular (in 10K increments) calibration curve. Intermediate values are interpolated by cubic splines.

For simultaneous measurement of luminescence and heat of heterogeneous reactions (adsorption, recombination), the luminophore sample under study is applied with a thin layer on the surface of a spiral-shaped wire detector 10 protected by SiO_2 film. In this case, the heat of heterogeneous reactions is determined by the method (Elias *et al.*, 1959).

Accurately linking the readings of the PT-thermometer of the substrate 6 or the resistive detector 10 to the surface temperature of the sample under study is performed using a precision infrared thermometer (M190 MIKRON INSRUM.CAMP.) With an error of $\leq 1\%$. Temperature control of the sample, or linear heating when removing the curves of thermally stimulated luminescence, is carried out by the filament current of the micro-furnace of the substrate 6 defined by source 9 (stabilized source HY-3005, or a special thermostat providing linear heating).

For photoexcitation (photostimulation) of the samples under study in the wavelength range of 230–1200 nm, an arc mercury-xenon lamp (L2482 HAMAMATSU) is used as the source 25, and a deuterium lamp (DDS – 30) in the region of 190-230 nm. Both lamps are powered by a constant stabilized current. The required spectral region of exciting radiation in the range of 190-1200 nm is highlighted by a high-aperture (1: 2.9 relative aperture) monochromator 24 (ML 44 SOLAR LS) equipped with a photo shutter with an iris diaphragm 23 for fast shutdown and adjustment of the output light flux.

Narrow-band luminescence spectra of samples in the visible region are recorded photoelectrically in the photon counting mode using high-precision (reproducibility $< 1\%$, resolution up to $3 \text{ \AA}$) of monochromator 30 (MDR 206 LOMO), working with PC 44 commands. – counting head 29 (H7467-01 HAMAMATSU), control is carried out with the PC 44 through the RS-232C serial interface. For recording and processing of spectra using its own software. In the process of scanning the monochromator passes through a selected range of wavelengths. At each step, the current wavelength, the intensity of the glow and the temperature of the sample are recorded. At the end of the spectrum registration in the automatic mode, the

wavelength and intensity of radiation are adjusted, taking into account the nonlinearity of the monochromator and the selectivity of the measuring path of the installation.

In the region of 350-1150 nm, the emission spectra of samples with a resolution of 1.5 nm are recorded by a wideband spectrometer on a CCD 31 (QE 65000 OCEAN OPTICS), also controlled by a RS 44. The device allows you to capture the full range of time from 10 ms (from sources of high brightness) to 10 min (threshold light fluxes) with a width of 50 μm in the entrance slit. The recorded spectra are programmatically corrected taking into account the hardware functions of the measuring path taken from the black body radiation (SI photograph lamp 6.5-50, $T_{\text{color}} = 2854 \text{ K}$) and spectral lamps (mercury-helium, neon).

The luminescence intensity kinetics are recorded using photoelectric devices 27: a photomultiplier (PMT – 84-3), the signal from which through a preamplifier (C7319 HAMAMATSU) is fed to a computer recording module 26 (ML-840 Power Lab 4/20 ADInstruments), or (at low intensities) – a photosensor module (H7468-01 HAMAMATSU), also mated with an IBM PC 44. Both devices can be alternately connected to the quartz window 2 through the filter cartridge cassette 28.

All fixed electrical signals: about the sample temperature (from multimeter 8), about the heat of heterogeneous reactions (from microcalorimeter 11), about the luminescence kinetics (from recording module 26 or photosensor module 27), about the luminescence spectrum (from photon-counting The heads 29 and the spectrometer 31) are fed to an automatized workstation (AWP), which is used to collect, process and visualize experimental data. AWP includes: personal computer 44, with installed boards – ADC, digital input-output, pulse counter; separate peripheral devices – monitor 45, printer 46.

Due to the necessity of simultaneous recording of several signals, synchronization of data reading between different devices, conversion of fixed digital information into the corresponding physical quantities, we developed software that allowed us to automate the recording and processing of all basic experimental data. Development environment – Borland C++ Builder 6. The software is controlled from under Windows 98, 2000, XP. Data recording is carried out in a format that allows

their further processing using standard packages (MathCad, MathLab, Maple). All the main graphic and digital information are presented visually on the monitor.

Section ab is in a vacuum of $5 \cdot 10^{-5} \text{ Pa}$; bc – in a beam of oxygen atoms $\text{O} (^3\text{P}_2)$ with a density of $8 \cdot 10^{16} \text{ cm}^{-2} \cdot \text{s}^{-1}$; cd – with the rapid overlapping of the oxygen beam, in a vacuum of $1 \cdot 10^{-4} \text{ Pa}$. To illustrate the effect of atomic-molecular beams on the luminescence of phosphorus in Fig. 2 and Fig. 3, fragments of the kinetics and photoluminescence spectrum of the disperse widely used in plasma panels are shown. $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, taken on the installation in a vacuum and in a beam of oxygen atoms.

CONCLUSIONS:

The obtained data on the regularities of the surface luminescence induced by oxygen and oxygen-containing particles open up new possibilities in the study of electronic and atomic-molecular processes on the surface of solids in the presence of a nonequilibrium gas atmosphere. This concerns both the elucidation of the mechanisms of excitation of surface luminescence centers and the establishment of the constants of individual stages of elementary interactions on the surface (adsorption, desorption, recombination, diffusion of gas particles, and the stoichiometric completion of the lattice).

The experimental setup allows us to study the laws of excitation, stimulation and quenching of the luminescence of a solid body that has the properties of crystal phosphorus, when exposed to its surface beams of gas particles (atoms, molecules) and on this basis. It helps to obtain data on atomic-molecular and electronic processes at the boundary between a solid and a non-uniform gas by luminescent-kinetic, calorimetric and spectroscopic methods.

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Figure 1. Experimental setup: 1 – vacuum chamber; 2-5 – optical windows; 6- substrate micro furnace; 7 – sample; 8 – multimeter B7-21A; 9 – current source HY-3005 (special thermostat); 10 – microcalorimeter detector; 11 – automatic microcalorimeter; 12,13 – glass nozzles; 14,22 – discharge tubes; 15,21 – RF generators; 16,20 – permanent magnets; 17 – trap of electronically excited molecules; 18,19 – Wood's light traps; 23 – photo shutter with iris diaphragm; 24 – high-aperture monochromator ML 44; 25 – source of photoexcitation H2482 (DDS-30); 26 – recording module ML-840; 27 – FEU-84-3 with a preamplifier C7319 (photo sensor module N7468-01); 28 – cassette with light filters; 29-photon-counting head H7467-01; 30 – diffraction monochromator MDR-204; 31 – QE 65000 CCD spectrometer; 32,33 – magnetic discharge pumps NMD-04, NMD-016; 34,41 – needle leak; 35,40 – Alcatel fore-vacuum pumps 2015; 36,39 – water cooled oil vapor traps; 37,38 – nitrogen traps; 42,43 – low pressure gas cylinders with MD-49-A man-vacuum meters; 44 – personal computer; 45 – monitor; 46 – printer

Figure 2. The photoluminescence kinetics of $\text{Y}_2\text{O}_3: \text{Eu}^{3+}$ (0.1% mass.) In a band with a maximum near 611.3 nm, excited by UV radiation of 5.90 eV, at a sample temperature

of 600 K

Figure 3. The photoluminescence spectrum of $Y_2O_3:Eu^{3+}$ (0.1% mass.) Excited by UV radiation of 5.90 eV at a sample temperature of 600 K. 1 – in a vacuum of $5 \cdot 10^{-5}$ Pa; 2 – in the beam of oxygen atoms with a density of $8 \cdot 10^{16} \text{ cm}^{-2} \cdot \text{s}^{-1}$, 30 minutes after the beginning of exposure to the beam