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On the mechanisms of formation of excited yttrium atoms under ion bombardment of yttrium and yttrium-aluminum garnet

I.A. Afanas'eva, V.V. Bobkov*, V.V. Gritsyna, I.I. Okseniuk, D.I. Shevchenko, I.S. Zelenina

V.N. Karazin Kharkiv National University, 61022 Kharkiv, Ukraine

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ABSTRACT

A comparison of the emission spectra of excited yttrium atoms ejected from the surface of the metal yttrium and yttrium-aluminum garnet (YAG) by Ar^+ ions with energy 20 keV to the emission spectra of excited yttrium atoms ejected from the surface of metal yttrium by Xe^+ ions with energy 40 keV has been made. A sharp increase of population states of yttrium atoms with low energy excitation ($z\ ^2D^\circ$, $z\ ^4F^\circ$) ejected both from metallic yttrium and YAG under Ar^+ bombardment was established when compared with the metallic yttrium bombarded Xe^+ ions. The spatial distribution of radiation of excited yttrium atoms ejected from yttrium and YAG by Ar^+ ions was measured. It showed that the yttrium atoms in the excited states $z\ ^2G^\circ$ and $z\ ^4F^\circ$ have low kinetic energy (order eV), whereas the yttrium atoms in other states have kinetic energy of order 100–300 eV and also more than 4 keV. It was proposed that, in addition to formation by a collision mechanism, there are low excited yttrium atoms due the break-up of yttrium oxide molecules in unstable electron states of excited yttrium and oxygen atoms.

1. Introduction

Under the bombardment of solids by ions with mid-keV energy secondary emission processes take place including scattering, sputtering, secondary ion, photon and electron emissions. The process of ion-photon emission (IPE) is connected with emission of electromagnetic radiation by ejected particles in excited states. The investigation of the main parameters of the IPE allow the important information on the processes of particles ejection, their excitation and conservation of this excitation at leaving the surface of solids to be obtained. Based on IPE the method of ion-photon spectrometry (IPS) is developed: it permits the data about the nature and amount of sputtered excited particles, their kinetic energy and determination of the particle distribution of the excited states to be obtained simultaneously. Although there are a large number investigations on IPE, there is no unique theory for the description of the processes of the excited particle formation under ion bombardment of solids. This is associated probably with the high complexity of the problem in which it is necessary to take into account all known parameters of solids and the spectroscopic parameters of ejected excited particles. Previous investigations of IPE on different materials show that the number processes of excited state formation of ejected particles increases with complexity of the target. Under bombardment of single-element solids (primary metals [1,2]) the collisional processes (multiple collisions or linear cascade collisions) with subsequent processes of electron exchange with solids lead to the formation of excited states of an ejected particle. Hence the band-structure of the solid is a very important parameter during formation of the ejected excited particle [1,3]. The adsorption of chemical active gases at the surface of the solid leads to an additional process of excited particle formation due to the rupture of molecular bonds [4]. For complex samples such as chemical compounds [5] and metal alloys [6] an essential additional contribution to the formation of the excited particles causes rupture of the chemical bonds. Studies in recent years have indicated that the probability of formation of excited states of the ejected particles substantially depends on the specific electron shell of the excited state [7–9] of the ejected particle. Therefore, to understand the mechanism of interaction of the medium energy ion with the surface of a solid and to develop the IPS method for solution of a number applied problems it is necessary to make further investigations of the main IPE parameters for different materials.

Yttrium Aluminum Garnet (YAG, chemical formula $Y_3Al_5O_{12}$) with a cubic garnet structure has received much attention due to its interesting optical and mechanical properties [10]. In particular,

* Corresponding author.
E-mail address: vbobkov@mail.ru (V.V. Bobkov).

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synthetic yttrium aluminum garnet, either pure or doped with active impurities such as Nd3+ or Ce3+, is used in a wide variety of applications, such as thermal coating, optical lenses, solid-state lasers and solid-state-lighting devices [10]. Hence investigations the response of YAG to ion irradiation and ion stimulated emission are very important. Also YAG is complex compound and by investigating its IPE additional information about formation excited particles under ion bombardment can be obtained.

We have studied the basic parameters (spectral composition, quantum yield and the spatial distribution of the radiation of ejected excited yttrium atoms) of IPE occurring when the surface of the metal (yttrium) or YAG is bombarded by Ar^+ ions. From the comparison of our experimental results and data from Ref. [8] conclusions about the mechanisms of formation of excited states of yttrium atoms and the influence on the probability of their formation the electron structure of a solid as well as the type of the electron shell of excited state of an ejected yttrium atom were made.

2. Experimental details

The studies were done using an experimental device with mass-separated beam of 20 keV Ar^+ ions and a current density of 15 $\mu A \cdot cm^{-2}$. The incident angle of the beam to the target was 45°, which corresponds to near the maximal value of sputtering coefficient. The vacuum in the target chamber was about 10^{-5} Pa (partial oxygen pressure was $5 \cdot 10^{-6}$ Pa), which was obtained by using oil pumps and liquid nitrogen oil traps.

The photon emission of the excited particles was measured in the direction perpendicular to plane created by bombarding beam and normal to target surface, so only the radiation of knocked out particles was investigated. The radiation of ejected excited particles was taken out through the quart glass window and focused with an achromatic long-focus lens (F = 14 cm) onto the entrance slit of the data collection and analysis system. A long-focus lens was placed so that the image of the light halo above the surface was decreased and was projected on that part of the entrance slit where the signal was linearly dependent on the number of photons. Such radiation collection geometry allowed the total number of photons emitted by particles knocked out from the surface in excited states to be measured.

The emission spectra in the range 250–800 nm were analyzed with monochromator MDR-3 (Optical Mechanical Association, St Petersburg) and registered using a cooled photomultiplier FEU-106 (Electro-Lamp Plant, Moscow) by photon counting. Calibration of sensitivity of the photon detection system was done with the help of a tungsten standard lamp. The special attachment on the entrance slit of MDR-3 can be used to move the slit 0.1 mm along the image of the light halo above the surface of the target and the distribution of radiation along the entrance slit can be measured.

3. Experimental results

In our previous work [11,12] the emission spectra of the particles knocked out from yttrium iron garnet (YIG) and YAG on bombardment by Ar^+ ions with energy 20 keV have been studied. A significant difference between these spectra should be noted. In the of YIG spectra intense spectral lines of iron and no lines of yttrium atoms (Y I) and ions (Y II) were seen. In the YAG spectra intense spectral lines of yttrium (Y I, Y II) and aluminum atoms (Al I) and ions (Al II) were seen. In addition the composition of spectra and distribution of intensity of lines in the spectra of both garnets differ from corresponding parameters for the metals: Fe for YIG and Al and Y for YAG.

To continue these investigations in this work only the data relating to the emissions of the excited atoms of yttrium knocked out from YAG will be considered. In Table 1 the quantum yield of the radiation (γ_λ) (the number of photons of the studied wavelengths per single incident ion) emitted by excited particles of yttrium ejected from YAG and the metal yttrium, as well as wavelengths of corresponding emissions and their interpretation, the electronic transition and the excitation energy of the upper state of the transition are given.

Analysis of the data presented in Table 1 indicates that, in the emission spectra of the particles ejected from the metal yttrium, there are Y I and Y II spectral lines, but the distribution of intensity in these spectra is different in comparison with ion bombardment of YAG. For Y I spectral lines, emitted by the yttrium atoms excited in states $z\,^2D^\circ$ and $z\,^4F^\circ$ with low excitation energies $E_{exc} < 2.0$ eV, an increase in the value of the quantum yield for YAG compared to Y is observed. For Y I spectral lines, due to transitions from highly excited states of yttrium atoms, there is practically no difference in the values of the quantum yields for YAG and Y. For the majority of Y II spectral lines, emitted by excited yttrium ions, there is an increase in the quantum yield for YAG in comparison with the metal yttrium. In addition, in the spectra of YAG and Y there are a number of cants of blue-green and orange system bands of the molecule YO, i.e. the transitions from $^2\Sigma$ and $^2\Pi$ excited states to ground state $^2\Sigma$ [13].

It is interesting to compare our results with the data of [8], where the emission spectra of the yttrium excited atoms sputtered by Xe^+ ions (40 keV, current density of 500 $\mu A \cdot cm^{-2}$, pressure 10^{-8} Pa) from the surface of the metal yttrium were studied. For estimating the influence of the presence of oxygen on the surface of targets in our experiment compared with the data for the clean surface of the metal yttrium [8] it is necessary to compare the number particles in state *i* which have knocked out one incident ion Ar^+ in our experiment (n_i^{Ar}) to (n_i^{Xe}) from Ref. [8]. Taking into account that $\gamma_\lambda = \gamma_{ik}$ the number n_i^{Ar} can be determined by relation [14]:

$$n_i^{Ar} = \gamma_{ik} \cdot b_{ik}^{-1}, \quad (1)$$

where b_{ik} – relative probability of transition *ik*, which defined as

$$b_{ik} = A_{ik} \cdot \left(\sum A_{if} \right)^{-1} = A_{ik} \cdot \tau_i \,, \quad (2)$$

where A_{ik} – the probability of transition *ik*, ΣA_{if} – the probability of all possible transitions from level *i*, τ_i – the lifetime of *i*-th state.

The intensity of the spectral line (*I*) defined in Ref. [8] is a radiant quantity and connect with n_i^{Xe} by the relation $I = n_i^{Xe} \cdot A_{ik} \cdot (hc/\lambda)$ [15], where h is the Planck constant and c the speed of light. So it is possible to compare (n_i^{Ar}) versus (n_i^{Xe}) using experimental data γ_λ and $I\lambda$. Figs. 1 and 2 show the dependences ratio $\gamma_\lambda / I\lambda$ on the energy of the excited state (E_{exc}) of the upper state of corresponding transition for the studied target (YAG and Y) in our case compared with values for the clean surface of yttrium in Ref. [8]. It is seen that for lower excited states a sharp increase in the ratio $\gamma_\lambda / I\lambda$ both for YAG and metallic yttrium take place for our experiment when comparing with the clean surface of yttrium [8].

To estimate the velocity of sputtered excited yttrium atoms the spatial distribution of radiation for a number of intense spectral lines Y I was measured according to the procedure described in Ref. [16]. Intensity of emission *I* at the distance *l* from the surface of the target is proportional to the number of emitting particles n_i. Using a spontaneous decay law for the excited state *i* and the relation between the effective velocity υ_{eff} of excited particles, the distance (*l*) of the emitting particle from the surface of the target and the time ($t = l/\upsilon_{eff}$) we obtain: