РАДІАЦІЙНА ФІЗИКА
RADIATION PHYSICS

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EFFECTS OF LITHIUM INSERTION INTO VANADIUM PENTOXIDE THIN FILMS. CONTINUUM RADIATION STUDY

Optical emission of $Li_{x(x=0.2,0.7,1.2)}V_2O_5$ has been studied during 5 keV Kr^+ ions bombardment. Continuous luminescence was observed in a broad wavelength range between 280 and 340 nm. Generally, the emission intensity was influenced by the quantities of lithium giving rise to transient effects as well as an increase in the line intensity. The experimental results suggest that the continuum emission depends on the nature of surface interaction between lithium and vanadium pentoxide and is very probably related to its electronic structure.

Keywords: sputtering, sol-gel, optical-emission, vanadium pentoxide, intercalation and deintercalation.

1. Introduction

Nowadays, lithium-ion batteries are the most applied technology in many factories such as hybrid electric vehicles [1], various portable electronic devices [2], and emerging smart grids [3]. The use of batteries is growing due to the environmental issues caused by the depletion of fossil energy resources.

However, many studies have been explored to improve the performance of vanadium-based electrode materials. In these topics, the performance and working mechanism of amorphous electrode materials are far less understood.

Moreover, it is well known that the intercalation of lithium into V_2O_5 layers leads to the occupation of originally empty conduction band states corresponding to 3d-shell. During the insertion of lithium, the shift of Fermi level and formation of surface dipole has been observed in amorphous $Li_xV_2O_5$ [4] and $Na_xV_2O_5$ [5] deposited by the physical vapor deposition technique.

Several recent studies have implemented vanadium oxides as the battery [6]. Zheng et al. prepared V_2O_5 as the battery-type electrode for hybrid supercapacitors [7]. They indicate that the increasing complexity of the structure leads to lower specific capacitance because of the higher degree of electrode polarization and higher resistance. Wang et al. synthesized V_2O_5 hollow spheres with triple double-walled shells. They show improved electrochemical performance compared to single-shelled V_2O_5 hollow microspheres as electrode materials for lithium-ion batteries [8]. Han et al. [9] found that Fe doping enhanced Li^+ diffusivity arising from the expansion of the 1D channel in the polyanion structure of $LiCoPO_4$. Li et al. [10] observed that the electrical conductivity of $LiCoPO_4$ increased three orders of magnitude via coating with uniform carbon film. Covering the $LiCoPO_4$ cathode with a thin layer of Al_2O_3 could greatly alleviate the capacity fading.

Generally, continuum emission observed in front of transition metal targets is believed to arise from excited atom clusters (including diatomic and triatomic) ejected from the solid surface in the sputtering process [11, 12]. The continuum radiation observed in the case of transition metals gives rise to a broadband continuum emission which is observed spatially at distances of a few millimeters in front of the target [13, 14]. The phenomenon depends on the presence of oxygen at the target surface and the collective deactivation of 3d-shell electrons remains a possible source. According to these authors, the continuum radiation is observed in the case of clean titanium and clean vanadium. It is found to be enhanced by the presence of oxygen, probably due to chemisorption. This enhancement can reach respectively a factor of 2 and 5 for titanium and vanadium.

In the present work, we present the results of an experimental study that highlights the continuum radiation spectra during 5 Kr^+ ion beam sputtering of $Li_{x(x=0.2,0.7,1.2)}V_2O_5$ and vanadium pentoxide. To elucidate the origin of the continuum, we re-recorded the spectra of these targets under the same conditions of bombardment, spatially at the base pressure of 10^{-7} Torr. The effect of lithium insertion in vanadium pentoxide is discussed.

2. Materials and experimental details

2.1. Materials

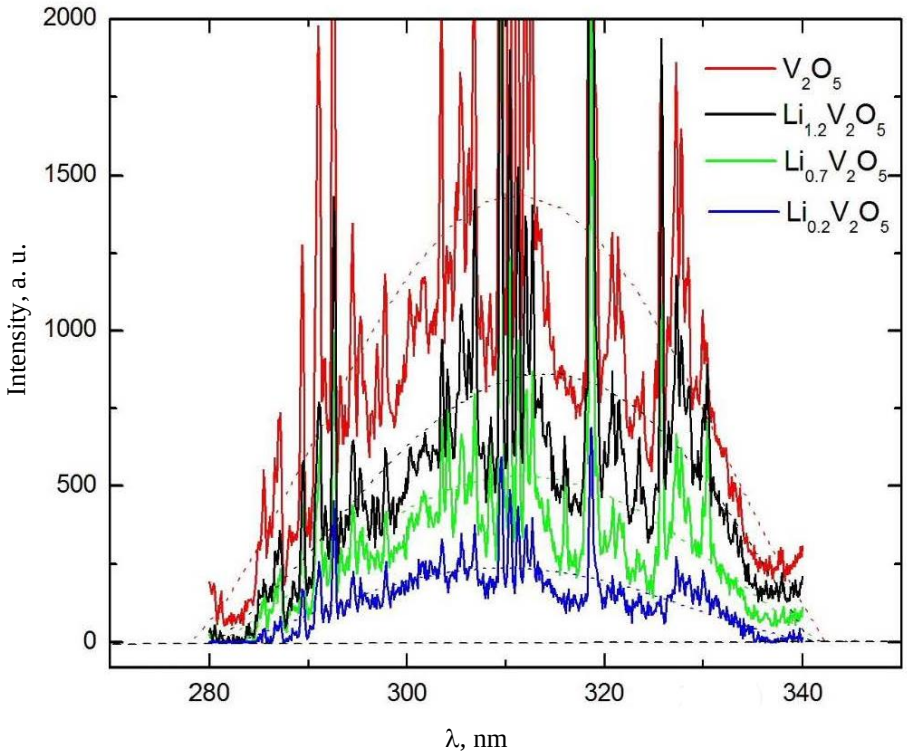
Thin films of V_2O_5 were prepared by sol-gel using the spin-coating method described in reference [15]. V_2O_5 soil was prepared by dissolving V_2O_5 powder with a solution of 15 % H_2O_2 under vigorous stirring. The layers were obtained by spin coating on a glass substrate of indium tin oxide which is then rotated at a speed of 2400 rev/min to a film thickness of 216 nm. The samples were subsequently undergoing a heat treatment at 150 °C for 1 h. Electrochemical measurements are carried out in a cell containing V_2O_5 film as a working electrode, a platinum electrode against a saturated calomel electrode (SCE) as a reference electrode, and a 1M solution of $LiClO_4$ in propylene carbonate as the electrolyte. Samples analyzed by the technical SIPS are four thin layers of V_2O_5: gross; polarized - 400 mV/(colored blue) and bleached to a polarization potential of 1200 mV/SCE.

2.2. Experimental details

The setup used in this work is a part of SIPS installed in our laboratory and described previously [16 - 18]. Briefly, Kr^+ ions with energies of 5 keV were produced by electron impact on Kr gas (of 99,998 % purity) in the plasma source. The ion beam is focused on a target mounted inside an ultra-high vacuum chamber. Vacuum is established by means of two turbomolecular pumps of 50 and 200 l/s capacities, respectively. In the absence of ionic bombardment, the residual pressure near the sample is less than 10^{-7} Torr. Prior to the start of each measurement, the targets were cleaned in situ by ion beam sputtering. The ion beam current was measured directly on the sample or by a Faraday cup placed behind the target, in the direction of the ion beam. The sample holder can rotate to change the angle of incidence between the ion beam and the normal to the sample surface and translate for consecutive analysis of several samples. The cross-section was 0.95 mm² given a fluence of 3.3 10^8 ion/mm². The incident angle was 60°. This angular position from the normal to the surface maximizes the sputtering yield and therefore the photon yield. The emitted light was analyzed through an R320 Jobin - Yvon monochromator equipped with 1800 groves/mm holographic grating using a 400 μm slit width. Hamamatsu 4220P photomultiplier is used to explore the wavelength range and a micro-computer is used with the PRISM program to control the whole detection system and to collect data.

3. Experimental results and discussion

Figure shows the partial optical spectrum of vanadium pentoxide and $Li_{x(x=0.2,0,7,1.2)}V_2O_5$ bombarded by 5 keV Kr^+. These samples are sealed in a vacuum chamber and examined under the same experimental conditions (Table 1).



Photon spectrum of clean V_2O_5 and $Li_{x(x=0.2,0.7,1.2)}V_2O_5$ films bombarded by 5 keV Kr^+ ions.
The dotted line is the best-fit curve for the continuum radiation. (See color Figure on the journal website.)

Table 1. **Experimental conditions of recording the spectra of luminescence by SIPS**

Vacuum in the target chamber	$< 10^{-7}$ torr
Monochromator slits	400 mm
Angles of incidence	70°
Wavelength range	200 - 300 nm
Spectral resolution	0.32 nm
Counting time	1000 ms
Sample current	0.5 - 0.6 mA
Ion's energy	5 keV

The observed spectra consist of a series of discrete lines superimposed on a broad continuum range between 280 and 340 nm. The most intense line is located at 318.7 nm and attributed to V I due to the $3d^3\ 4s^2\ ^4F_{1/2}$ - $3d^3\ 4s\ 4p\ ^4G_{1/2}$ transition.

The measured photon intensities are very higher for clean V_2O_5 compared to the intercalated Li^+ ions. This behavior observed is probably caused by the changes in the electronic structure of $Li_xV_2O_5$ by the formation of surface dipole which leads to a strong shift in the Fermi level.

In the recorded spectra, the height of continuum radiation decreases with the insertion of lithium in the vanadium pentoxide. This decline can reach a factor of 2 probably due to the chemisorptions phenomenon. The solvent used during synthesis was found to play a critical role in structure formation based on the chemisorption of preferred molecules [19]. J. Yao et al. [20] focused on selected topics covering the influences of surface chemistry, crystallinity, doping, defects, and nanostructures on the lithium-ion intercalation properties and recent developments on other metal batteries including NIBs and MIBs. For vanadium pentoxide, the collective deactivation of 3d-shell electrons appears to play a role in the emission of this radiation. Noted that this is the radiation of the knocked-out particles.

We simulated a broad-band continuum to a discrete line (see Figure). The full widths at half maximum (FWHM) (Table 2) are almost identical (37.80, 38.49, 38.15, and 38.84 for respectively $Li_{0.2}V_2O_5$, $Li_{0.7}V_2O_5$, $Li_{1.2}V_2O_5$, and clean V_2O_5). The same phenomena were observed by Jadoual et al. [21]. They suggested that the lifetime of the continuum radiation is similarly identical in the case of titanium and Ti + O_2 structures. As a result, the origin of the continuum radiation is probably the same for titanium and the structure formed in the presence of oxygen (Ti + O_2). On the other hand, we suggest that the observed continuum radiation is due to the excited-state formation for Me-A molecules (where Me is an atom of transition metal with partly occupied d electron shells; A is an atom of reactive gas). Noted that the insertion of lithium decreases the effect of the continuum. It has been proposed that a molecule being sputtered without dissociation from the metal surface is excited beyond the region of effective electron exchange with the surface due to the transfer of kinetic energy of relative motion of the nuclei to the electron subsystem. Within the framework of this excited-state formation model, where de-excitation processes such as resonance ionization seem to be unlikely, it is possible to explain the main features observed in the continuum radiation.

Table 2. **The FWHM**

Sample	$Li_{0.2}V_2O_5$	$Li_{0.7}V_2O_5$	$Li_{1.2}V_2O_5$	V_2O_5
Maxima of the continuum	235 nm	535 nm	860 nm	1440 nm
FWHM	37.80 ± 1.5 nm	38.49 ± 1.5 nm	38.15 ± 1.5 nm	38.84 ± 1.5 nm

Table 3 shows the absolute intensities of observed lines in the case of the bombardment of clean V_2O_5 and $Li_{x(x=0.2,0.7,1.2)}V_2O_5$ films. The measured wavelengths of V I and V II lines and those given in the literature are denoted by λ_0 and λ_L, respectively [22, 23]. The difference between λ_0 and λ_L due to the calibration of the monochromator is approximately a constant value (0.2 nm). The second column lists the intensities of clean V_2O_5 and $Li_{x(x=0.2,0.7,1.2)}V_2O_5$ films. The identification of the transition responsible for the emission is given in the last column. Noted that no emission from sputtered excited atomic lithium was observed in the explored wavelength range.

The optical radiation, both from knocked-out particles and radiation arising from the luminescence of a solid body, enters the input slit of the optical device. Noted that the surface of the target is visible from the entrance slit, so the luminescence from the surface will affect the radiation spectrum.

The origin of this type of emission is largely discussed by several authors and none of the proposed models explains experimental observations. It was first observed by Tolk, While, and Sigmund and by Van der Weg and Lugujjo [24], and its origin is largely discussed. Kiyan, Gritsyna, and Fogel [25] advanced the hypothesis that it is the result of emission from sputtered atoms in which the atomic electron shell (the incomplete d-or-f-shell) is excited collectively as a result of a collision at the surface. White, Tolk, Kraus, and Van der Weg [26] as well as Kerkdijk, Schartner, and Saris [27] concluded that the emitting species are probably excited neutral metal molecules and have suggested sputtered metal di- and

Table 3. **Identification of the main lines observed in the region 280 - 340 nm during the bombardment of clean V_2O_5 and $Li_{x(x=0.2,0.7,1.2)}V_2O_5$ films by 5 keV Kr^+ ions**

λ_0, nm	λ_L, nm	Intensity, a. u.				Transition
		V_2O_5	$Li_{0.2}V_2O_5$	$Li_{0.7}V_2O_5$	$Li_{1.2}V_2O_5$	
289.4	289.42 V II	1231	558	462	137	$3d^34s$ a $^5F_4$ - $3d^34p$ z $^5D_3$
291.1	290.97 V II	1926	762	627	248	$3d^34s$ a $^5F_5$ - $3d^34p$ z $^5D_4$
292.6	292.49 V II	2962	1429	1002	449	$3d^34s$ a $^5F_5$ - $3d^34p$ z $^5F^\circ_5$
294.5	294.54 V II	1335	643	432	192	$3d^34s$ a $^5F_4$ - $3d^34p$ z $^5F_3$
295.3	295.29 V II	1033	552	346	182	$3d^34s$ a $^5F_3$ - $3d^34p$ z $^5F_2$
305.5	305.72 V I	1769	1089	642	328	$3d^34s^2$ a $^4F_{5/2}$ - $3d^34s4p$ w $^4F_{5/2}$
306.9	307.05 V I	2360	1437	781	362	$3d^34s^2$ a $^4F_{7/2}$ - $3d^34s4p$ x $^4D_{7/2}$
308.4	308.30 V I	1093	692	642	218	$3d^34s^2$ a $^4F_{9/2}$ - $3d^34s4p$ w $^4F_{7/2}$
309.5	309.41 V I	4720	2721	2213	543	$3d^34s4p$ x $^4D_{3/2}$ - $3d^34s^2$ a $^4F_{5/2}$
310.4	310.18 V II	3439	1879	1209	497	$3d^34s$ b $^3G_3$ - $3d^34p$ y $^3G_3$
311.3	311.39 V IV	2338	1407	914	393	$3p^63d4d$ $^3F_3$ - $3p^63d5p$ $^3D_2$
312.1	312.22 V IV	2173	1297	804	339	$3p^63d4d$ $^3F_2$ - $3p^63d5p$ $^3D_1$
318.7	318.63 V I	6283	4832	2258	697	$3d^34s^2$ a $^4F_{9/2}$ - $3d^34s4p$ x $^4G_{11/2}$
320.8	320.83 V I	1272	834	423	176	$3d^34s^2$ a $^4F_{9/2}$ - $3d^34s4p$ x $^4G_{9/2}$
321.5	321.34 V I	1148	709	408	189	$3d^34s^2$ a $^2G_{9/2}$ - u $^2H_{11/2}$
327.3	327.20 V II	1841	1147	640	279	$3d^34s$ a $^3F_3$ - $3d^34p$ z $^3G_4$
327.8	327.70 V II	1643	977	601	225	$3d^34s$ a $^3F_4$ - $3d^34p$ z $^3G_5$

polymer molecules as a source of the continuum emission. Rausch et al. [28] suggested that emission from oxide molecules is responsible for the continuum. Vege [29] attributed the continua to the chemiluminescence due to oxygen reacting with the target surface. A similar chemiluminescence model of broad-band optical radiation has been proposed by Bazhin et al. [30]. Van der Weg et al. [24] observed continuum radiation from some metals during 40 keV Ar^+ bombardment, this included weak radiation from silicium and strong from titanium, chromium, zirconium, molibdenum, tantalum, and tungsten, and no radiation from nickel, copper, palladium, silver, and platinum. However, other authors did not report continuum radiation, under circumstances where they should have observed it according to refs, Tsong [31] did not observe continuum radiation from tantalum, vanadium, and tungsten, probably because of his optical having a very low sensitivity, Terzic et al. [32] detected only spectral lines from molybdenum under 40 keV Ar^+ bombardment. Stuart and Wehner [33] did not report continuum radiation from molibdenum, but the experimental conditions were different from the setup usually used in bombardment-induced photon emission studies. Kerkow [34] bombarded, amongst others, tantalum, tungsten, molibdenum, iron, and chromium with 10 keV K^+ and Cs^+, but did not report continuum radiation. Jensen and Veje [35] bombarded titanium with 50 keV Xe^+ but the observation of continuum radiation was not reported.

4. Conclusion

Bombardment-induced light emission of clean V_2O_5 and $Li_{x(x=0.2,0.7,1.2)}V_2O_5$ films were studied. The percentage of lithium insertion in the vanadium pentoxide decreases the intensities of the observed spectral lines and the continuum as well. The collective deactivation of 3d-shell electrons appears to play a role in the emission of this radiation in the case of vanadium pentoxide. The observed decreases in the insertion of lithium are probably due to a significant contribution of the Electrochemical chemisorption between lithium and vanadium pentoxide. Other experiments must be conducted to further elucidate the origin of this radiation.

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ВПЛИВ ДОДАВАННЯ ЛІТІЮ В ТОНКІ ПЛІВКИ ПЕНТОКСИДУ ВАНАДІЮ. ДОСЛІДЖЕННЯ НЕПЕРЕРВНОГО ВИПРОМІНЮВАННЯ.

Досліджено оптичне випромінювання $Li_{x(x=0,2,0,7,1,2)}V_2O_5$ під час бомбардування іонами Kr^+ з енергією 5 кеВ. Неперервна люмінесценція спостерігалася в широкому діапазоні довжин хвиль від 280 до 340 нм. Як правило, на інтенсивність випромінювання впливала кількість літію, що викликало перехідні ефекти, а також збільшення інтенсивності ліній. Експериментальні результати свідчать про те, що неперервне випромінювання залежить від характеру поверхневої взаємодії між літієм і пентоксидом ванадію і, ймовірно, пов'язане з його електронною структурою.

Ключові слова: напилення, золь-гель, оптична емісія, пентоксид ванадію, інтеркаляція і деінтеркаляція.

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