Room temperature photo-induced, Eu^{3+}-doped IGZO transparent thin films fabricated using sol–gel method

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Abstract

Red-emitting Eu^{3+}-doped indium gallium zinc oxide (IGZO) transparent thin films were fabricated using sol–gel method under UV (254-nm irradiation) in nitrogen atmosphere (inside the glove box) and thermally annealed at 500°C for 1 h. Structure, morphology, composition, and optical properties of the materials were examined using X-ray diffraction analysis, scanning electron microscope, X-ray photoelectron spectroscopy, and photoluminescence, respectively.

Keywords

Oxides, Annealing, Photoelectron spectroscopy, Luminescence

Background

Transparent semiconducting oxides have received greater attention because of their wide range of applications in active matrix electronics, displays, sensor arrays, and X-ray detectors [1-5]. It is well established that the indium gallium zinc oxide (IGZO) is transparent to visible light and has higher electron mobility than the conventional amorphous semiconductors, (e.g., amorphous silicon) and has higher switching speed, better electronic stability, more transparent displays, and more flexible electronics [6,7]. During recent years, solution-based synthesis materials have got more interest due to their excellent optical transparency and as new prospects for low-cost, high-throughput, easy-compositional modification and as printable and transparent electronics devices [1,8-10].

For a long time, the conventional sol–gel method is used to grow thin films by the coating of wet precursors followed by thermal annealing at higher temperatures for their decomposition and oxidation [8]. Recently, Kim et al. [1] have developed a new photochemical activation induced by deep-ultraviolet light from a low-pressure mercury lamp in an inert atmosphere (to prevent reactive ozone formation) to achieve high degrees of sol–gel condensation and film densification in amorphous metal oxide semiconductor systems. Unfortunately, there are no reports available on the rare-earth-doped IGZO solution-based synthesis. Normally, rare-earth materials are the noble candidates for optically active ions in semiconductor materials because they show many absorption and fluorescence transitions in the almost visible region. Rare-earth materials have additional significant features in contrast to other optically active ions as well: the wavelengths of their emission and absorption transitions are moderately unresponsive to host materials; they have longer lifetimes of energy states, higher quantum efficiency and good color rendering index [11,12], which lead to their excellent performance in many optoelectronic applications. Recently, Muth et al. [13,14] have developed the transparent europium-doped IGZO thin film for electroluminescent (TFEL) device using the integrated circuits that were fabricated using pulsed laser deposition (PLD). To the best of our knowledge, no systematic study has been carried out on the rare-earth-doped IGZO using sol–gel thin films.

With this aim, we prepared rare-earth-doped IGZO using sol–gel thin films. Our synthesis work on IGZO:Eu^{3+} has a similar route to that of Kim et al. [1], but there is a slight modification in the UV annealing treatment which is explained below. In this work, we have prepared the transparent IGZO:Eu^{3+} sol–gel thin films under UV (254-nm irradiation) [under nitrogen atmosphere (all the UV curing treatments were carried out inside the glove box)] and thermally annealed (500°C, 1 h) for comparative investigation. The selection of high-energy UV lamp (254 nm) is the alternative source for chemical cleavage and rearrangement of disordered M–O–M networks under room temperature UV treatment instead of high-temperature annealing, which results in the preparation of high-quality IGZO:Eu^{3+} thin films. The structure and phase purity of the samples were analyzed using X-ray diffraction pattern. The scanning electron microscope (SEM) images of IGZO:Eu^{3+} film confirm that the smaller nanocrystalline grains are homogenously dispersed in the elaborated thin films. The elemental and compositional analysis using X-ray photoelectron spectroscopy (XPS) confirms the presence of In, Ga, Zn, O, and Eu. The room temperature photoluminescence emission properties of IGZO:Eu^{3+} films were studied in detail.

Results and discussion

Structure and morphology of IGZO:Eu^{3+} thin films

In Figure 1, the IGZO:Eu^{3+} films that are post-annealed at 150°C show an amorphous phase, while the film with the annealing temperature at 450°C exhibits a less polycrystalline phase with (009) and (104) peaks as investigated by X-ray diffraction (XRD) measurement. Subsequently, the as-spun films were ultraviolet-treated (254 nm, 90 min) under N_2 atmosphere which also exhibits the similar behavior. No other additional peaks of impurity were observed. Furthermore, the SEM images of IGZO:Eu^{3+} film confirm that the nanocrystalline grains are homogenously dispersed in the elaborated thin films (thickness of 50 to 70 nm) with an average size of 10 nm as seen in Figure 2a,b.

Figure 1 X-ray diffraction of thermal and UV-annealed IGZO:Eu^{3+} thin films.

Figure 2 SEM image of (a) thermal and (b) UV-annealed IGZO:Eu^{3+} thin films.

X-ray photoelectron spectroscopy

Figure 3 shows the XPS spectra of as-synthesized IGZO:Eu^{3+} thin films [UV-irradiated and thermally annealed (at 450°C)]. From the XPS analysis, it is observed that the presence of the core levels of In, Ga, Zn, O, and Eu in IGZO:Eu^{3+}thin films obtained are in the ranges of 100 to 300 eV (Zn 3*d* at 3 eV; In 3*d* at 17 eV; Zn 3*p* at 81.5 eV; Zn 3 s at 133 eV), 300 to 700 eV (In $3d_{5/2}$ at 444 eV; In $3d_{3/2}$ 452 eV; O 1 s 530.7 eV; In $3p_{3/2}$ at 665 eV; In $3p_{1/2}$ at 703 eV), and 800 to 1,200 eV (Zn $2p_{3/2}$ at 1,022 eV; Zn $2p_{1/2}$ 1,044 eV; Ga $2p_{3/2}$ at 1,117 eV; Ga $2p_{1/2}$ 1,144 eV; Eu $3d_{5/2}$ at 1,125.6 eV; Eu $3d_{3/2}$ at 1,152 eV). The binding energy data of IGZO:Eu^{3+} thin films are calibrated using carbon (1 s, 283.5 eV) as the reference. The line shape and peak positions are in good agreement with the literature [15].

Figure 3 X-ray photoelectron spectroscopy of thermal and UV-annealed IGZO:Eu^{3+} thin films.

Photoluminescence studies of IGZO:Eu^{3+} thin films

As can be seen in Figure 4, the photoluminescence (PL) emission spectra show the Stark splitting pattern of $^5D_0 \rightarrow {}^7F_J$ (J = 1–4), intra-configurational *f-f* electronic transitions of Eu^{3+}-doped IGZO UV, and thermally annealed thin films. Upon excitation with 254-nm UV irradiation, the emission spectrum is dominated by the hypersensitive red emission, showing a transition $^5D_0 \rightarrow {}^7F_2$ (due to electric dipole transition) which is stronger than $^5D_0 \rightarrow {}^7F_1$ (magnetic dipole transition). These transitions are known to be hypersensitive to the crystal structure and chemical surroundings. The presence of electric dipole transition confirmed that Eu^{3+} ions were located at sites without inversion symmetry (C_{3v} symmetry). The other transitions of $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$ were relatively very weak for all the samples. From the emission spectrum, it is seen that the transition $^5D_0 \rightarrow {}^7F_2$ is predominating for all the samples and it indicates that higher energy levels were coupled to ligand to metal stretching vibrations. The presence of strong luminescent intensity from trivalent europium ion (Eu^{3+}) in the IGZO matrix has intricate energy levels with energy gaps of various magnitudes. The optical property of the IGZO:Eu^{3+} thin film is in good agreement with the literature [12,13], which was obtained by PLD. The result envisages an effective route to synthesize IGZO:Eu^{3+} thin film and has a potential application in TFEL display devices, flexible transistor, and solar cell systems.

Figure 4 Photoluminescence emission spectra of thermal and UV-annealed IGZO:Eu^{3+} thin films.

Conclusions

In summary, we have fabricated amorphous IGZO:Eu^{3+} thin films on glass substrates by using a spin-coating method and studied the structure, composition, and optical property dependences of the UV and thermally annealed IGZO:Eu^{3+} thin films. The elemental and compositional analysis (XPS) confirms the presence of In, Ga, Zn, O, and Eu. The photoluminescence properties of IGZO:Eu^{3+} were thoroughly investigated and these materials have potential application in the display devices.

Methods

Synthesis of rare-earth (Eu^{3+})-doped IGZO thin film

All chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA). The precursor solution of IGZO:Eu^{3+} was prepared by dissolving zinc acetate dihydrate ($Zn(CH_3CO_2)_2 \cdot 2H_2O$), gallium nitrate hydrate ($Ga(NO_3)_3 \cdot xH_2O$), and indium nitrate hydrate ($In(NO_3)_3 \cdot xH_2O$) in 2-methoxyethanol (2-ME) solvent. The precursors were mixed at an millimolar concentration of In/Ga/Zn/Eu = 0.045:0.0125:0.0275:0.02 in the final oxide films. Then, 2.0 M of monoethanolamine (MEA) was added as a sol stabilizer, and acetic acid CH_3COOH was dropped to make a homogeneous solution while stirring. After vigorously stirring at 80°C for 5 h, the IGZO:Eu^{3+} sol was subsequently aged for 1 day before spin coating. The IGZO:Eu^{3+} thin films were spin-coated on the substrates (0.7-mm-thick glass) with spin rotation speeds of 3,000 rpm for 30 s. The light-induced photochemical treatment was performed using a high-density ultraviolet treatment (254 nm) in N_2 atmosphere inside the glove box. Upon UV annealing process, the radiant thermal energy of UV lamp increases the surface temperature of the substrate to 110°C to 120°C. The output energy intensity of the lamp was 20 to 23 mW cm^{-2}. The total energy delivered to the sample surface is calculated to be approximately 125 J cm^{-2}. For comparative investigation, the as-spun films were thermally annealed at 500°C for 1 h.

Characterization

The XRD patterns were recorded using Philips X'Pert PRO PanAlytical diffractometer (PanAlytical Instruments, Almelo, the Netherlands) with CuKα radiation (λ = 0.15406 nm) at a scanning rate of 5° min^{-1}. The SEM measurements were carried out using FESEM JSM-7600 F. The XPS measurements were performed using a LAS-3000 surface analysis system (RIBER, Paris, France) employing AlKα X-rays (1,486.6 eV, width 0.5 eV). Room temperature PL spectra were recorded using Horiba-Jobin Yvon Fluromax-4P bench-top spectrofluorometer (HORIBA Instruments, Kyoto, Japan).

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

RK synthesized the materials and carried out all the characterization studies. JT participated in the sequence alignment, drafted the manuscript, and conceived of the study and participated in its design and coordination. RC participated in the sequence alignment. All authors read and approved the final manuscript.

Acknowledgments

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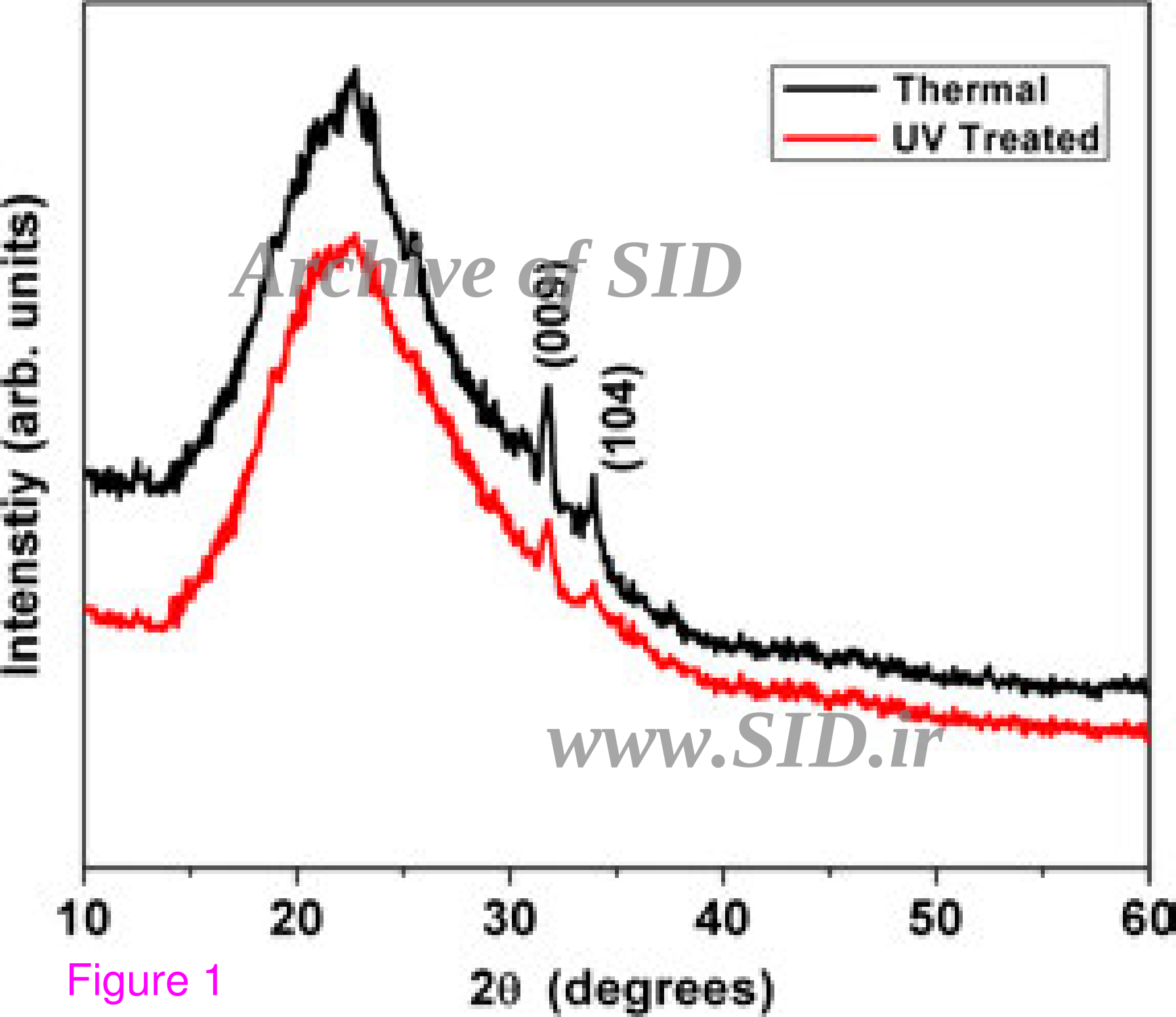

Figure 1

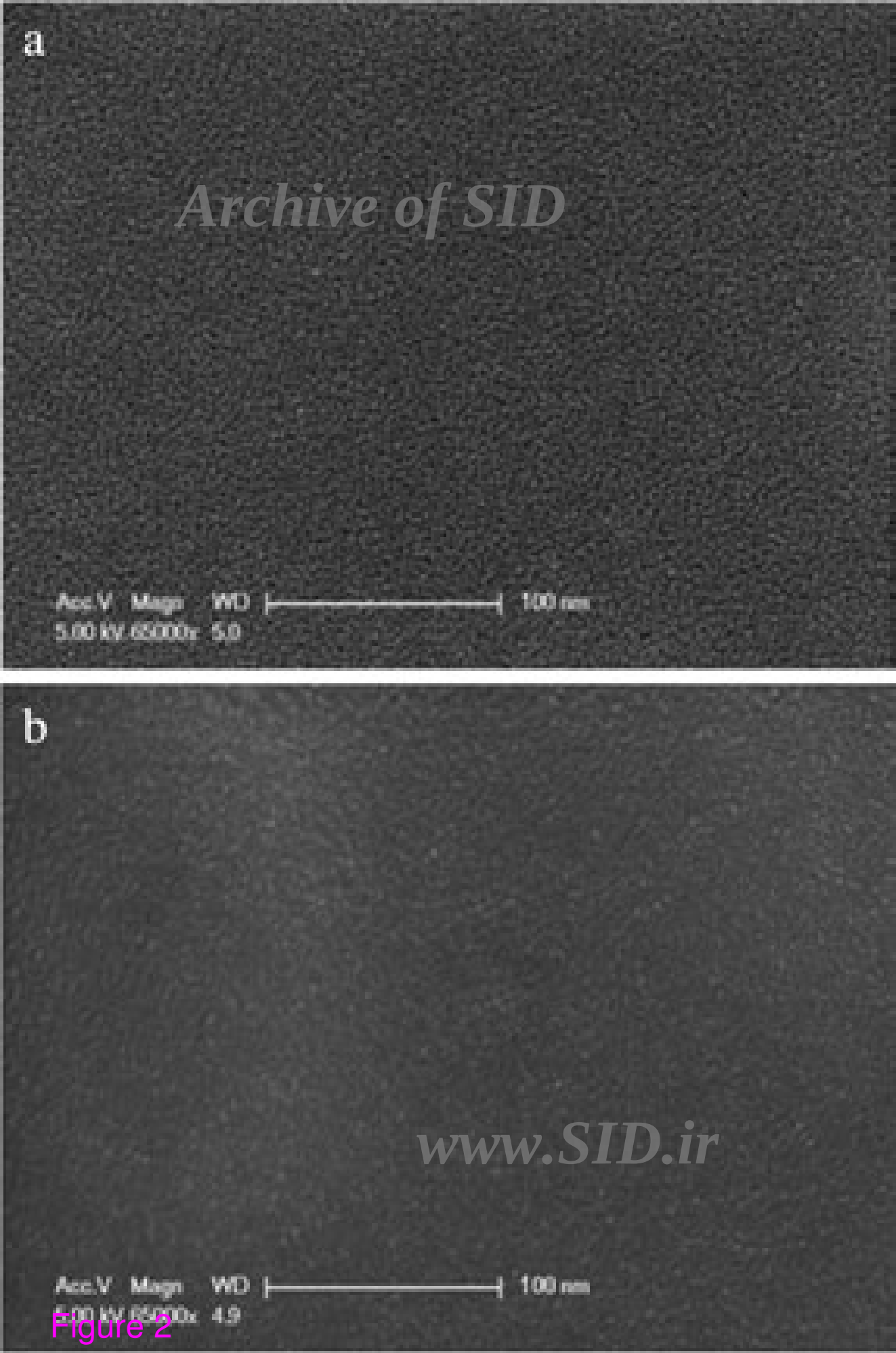
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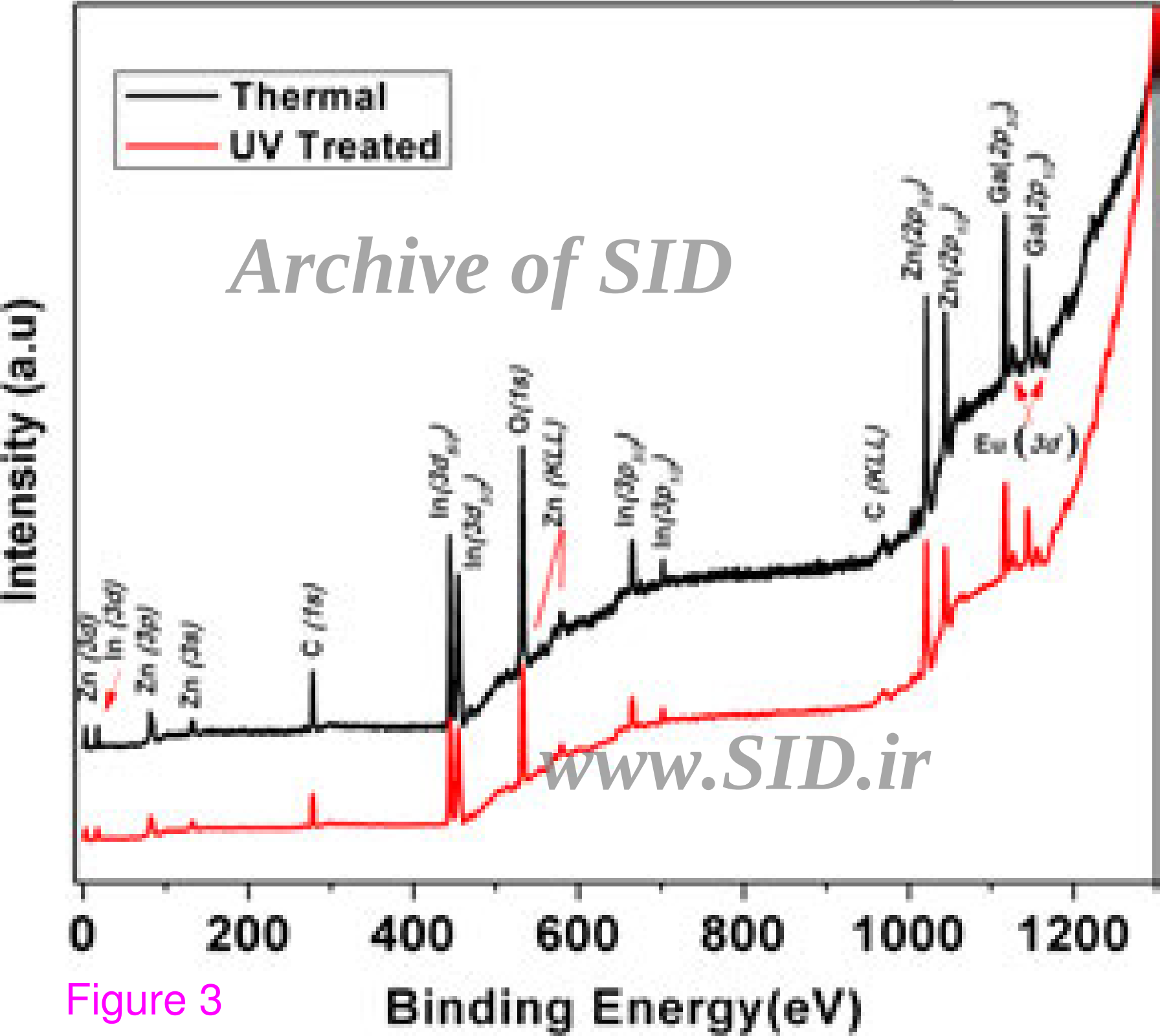
Figure 2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C (1s)
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In(3d5/2)
O(1s)
Zn (KLL)
In(3p1/2)
In(3p3/2)
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Eu (3d)

Figure 3

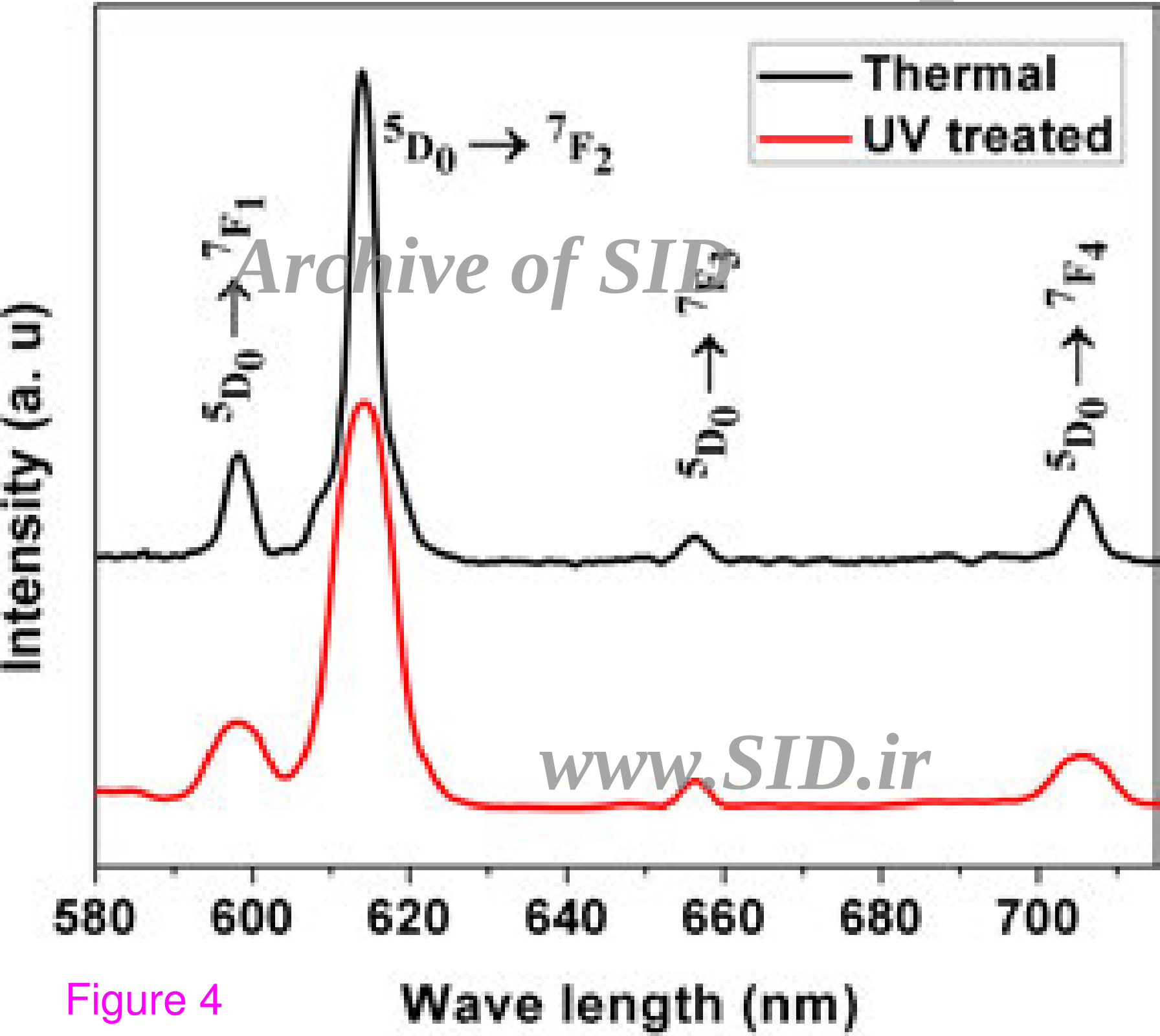

Figure 4

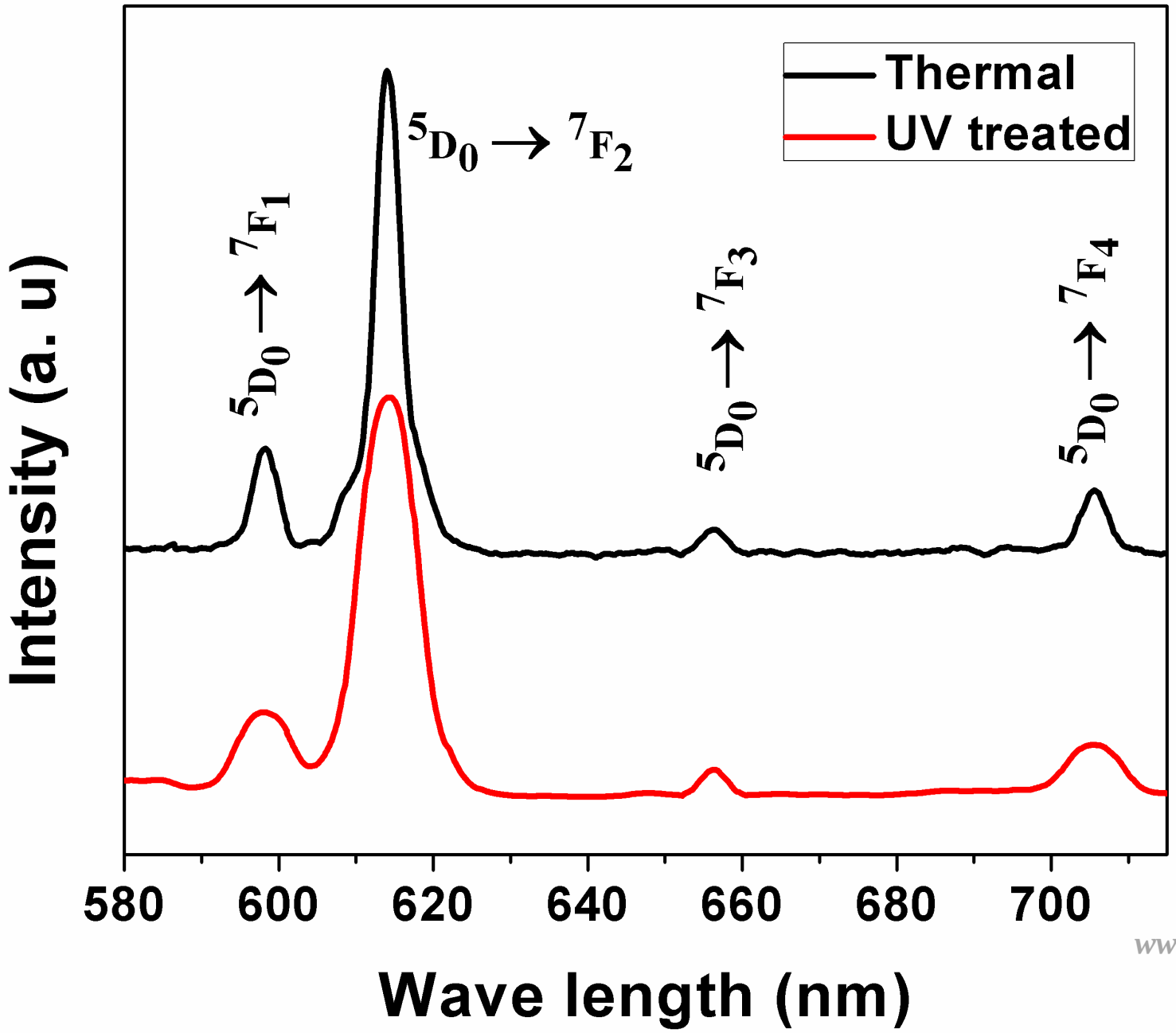

Figure 5