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Silicon oxynitride nanofilms prepared by PLD with controlled Eu-local concentration for broadband white light emitters

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ABSTRACT

We report the successful preparation and characterization of active silicon oxynitride thin films with controlled europium (Eu) doping by alternated pulsed laser deposition. The successful Eu doping with a nanostructured dopant distribution, as well as the stoichiometry of the oxynitride film, have been determined by ion beam analysis (RBS). The oxidation state of the incorporated Eu ions has been determined by in-depth x-ray photoelectron spectroscopy (XPS) and it is shown that the Eu ions are in the 2+ state, in contrast to the usual results found in oxide matrices for which the 3+ oxidation state prevails. The Eu-doped films show an intense broadband emission (FWHM >210 nm) associated to the optical transition $^4f_6^5d_1 \rightarrow {}^8S_{7/2}$ of the Eu^{2+} ions within the amorphous matrix. As expected, the intensity of the emission band increases as the Eu concentration increases, and it is remarkable that the emission shifts towards longer wavelengths. In terms of the chromatic coordinates (CIE) this implies a color tuning from a bluish to orange that enables color tunable emission, and potential white like emission by combining layers with different Eu^{2+} ions concentration. Therefore, the developed oxynitride films with controlled Eu^{2+} ions concentration achieved by PLD are promising for the development of color -tailored LED's.

1. Introduction

Nowadays the commercial solid state lighting based on rare earth doped powders or glasses for white-like emission are still predominantly preferred for manufacturing at large scale [1,2]. These phosphors are commonly categorized in distinct groups based on their host system chemistry: aluminates [3], silicates [4,5], phosphates [6], sulfates [7,8], fluorides [9,10], and oxynitrides with low FWHM centered around a specific color, i.e. β-SiAlON:Eu (green) [11], (Ca,Sr)$AlSiN_3$:Eu (red) [12], (Sr,Ba)$_2Si_5N_8$:Eu (red) [13], (Ca,Sr,Ba)$Si_2O_2N_2$:Eu (green) [14]. All of the above encourage for technology to move towards the nanoscale and nanostructuring of thin films. Furthermore, Eu^{2+} ions are so sensitive to the environment that they exhibit tunable properties when subjected to external mechanical pressures, extending their application as sensors [15]. In this context Si-based thin films like SiOC [16,17],SiO_x [18,19], have shown to be very promising to developed electroluminescent LED components with potential for integration in CMOS technology. These films showing either red emission or a broad white emission obtained from the reduction of Eu^{3+} (red) to Eu^{2+}(broad) upon the formation of Eu-silicates [20–23]. After a detailed study of photoluminescence and stoichiometry correlation in pure EuO_x thin films, the incorporation of europium ions in oxynitride matrices such as SiAlON, would be highly desirable. Oxynitride based materials are very attractive given its versatility due to several properties such as excellent mechanical properties, inertness, crystalline phase and chemical stability, high refractive index and tunable composition for desired applications [24,25], i.e.: solid state white emitters. Chemically they are also attractive since nitride films have been usually associated to formation Eu oxidation in the 2+ state, while in oxides tends to dominate the oxidation in the 3+ state. Thus, potentially combination of the two oxidations states can be achieved in oxynitrides [26,27,28,29]. In particular, the emission emerging from the Eu^{2+} has attracted great attention because it can be spectrally modified since it is originated from optical transitions from the 5d levels whose energy position is influenced by the crystal field splitting, the nature and the coordination number of the dopant ion as well as the arrangement and the nature of the ligands.

It has been reported previously that changes in the perceived color

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emission can be achieved by using a suitably combination of phosphors with different rare-earth emitters [30,31]. Indeed, this is a possible route for tailoring the emission of the films and we have already reported the preparation of SiAlON thin films doped either with Er^{3+} and Eu^{2+}, showing in each case NIR [32] or visible [26,33] emission, respectively. However, in this work we propose to explore the tuning of the emission with a single dopant. The idea is based in the fact that often in nitrides, in contrast to oxides, the crystal filed splitting around the embedded Eu^{2+} ion is higher, and this reduces the energy of the 5d orbitals and often results in red-shifted excitation and emission energies. Due to this there is an active search of new luminescent substances including different elements that enable changes of the Eu^{2+} 5d levels [27]. Following this approach we have prepared oxynitride thin films with locally controlled Eu content by means of the alternate deposition of a SiAlON host matrix and the Eu dopant. The nanostructured Eu-doped films show an excellent optical performance with a high intensity broadband emission that is solely related to Eu^{2+} ions, as shown by XPS analysis, and their spectral emission and correlated color temperature (CCT) show tuning as a function of the local Eu concentration. The obtained results suggest that the emission wavelength shift is related to a local environment change of the Eu ions and the 2+ oxidation state stabilization, and does not seem to be due to a reduction of Eu^{3+} as reported previously [34,35]. These results open up new opportunities for the development of lighting components based on single doped Eu SiAlON based compounds.

1.1. Experimental details

The thin films were prepared via pulsed laser deposition (PLD) using an ArF excimer UV laser ($\lambda = 193$ nm, 20 ns pulse duration) at a fluence of 4.10 J/cm^2. The deposition was carried out in a vacuum chamber equipped with several targets that can be selected alternatively for ablation. All the experiments were performed at vacuum 1×10^{-4} Pa and the substrate was kept at room temperature. The multilayer Eu-doped films were produced by the independent and alternate ablation of SiAlON_101 (target from Int. Syalons Co.) [36] and metallic europium 99.9% targets. The growth procedure that enables the controlled nanometric distribution of the rare-earth ions has been described in detail elsewhere [26,33,37,38]. Briefly, the films studied in this work where prepared by applying 360 pulses on the SiAlON target to deposit a 2.5 nm thick layer, and then to achieve the doping 10, 20 or 40 pulses were applied on the europium target. This deposition sequence SiAlON-layer/Eu-doping was repeated 60 times. Finally, a 25 nm capping layer was deposited to protect the last Eu-SiAlON layer from the ambient. Using this procedure, the films were designed to have a total thickness of 150 nm. For reference purposes films with no Eu doping were deposited under the same conditions. In order to optimize the emission performance, the films were subjected to thermal annealing in air up to 700 °C, in steps of 100 °C for 1 h in each step. The as-deposited and thermally treated SiAlON Eu-doped films were determined to be amorphous from Raman and XRD measurements that showed no crystalline modes or RX structures in the corresponding spectra [33]. In addition the structure of undoped SiAlON films has been studied by transmission electron microscopy that also confirms that they are amorphous [39]. Spectroscopic ellipsometry (SE) measurements were carried out in the 275–900 nm (1.38–4.51 eV) wavelength range at incidence angles of 65°, 70° and 75° using a VASE ellipsometer (J.A. Woollam Co., Inc.) in order to determine the dielectric function of the films and thickness. The ellipsometric Ψ and Δ values have been fitted to obtain the complex refractive index $\mathbf{n} = n + ik$ using a Cauchy function for the real part of the refractive index (n) and an Urbach absorption tail for the imaginary part of the refractive index (k) values. The atomic composition of the films was obtained by Rutherford backscattering spectrometry (RBS) measurements. The RBS spectra were acquired with ^{4}He at 2 MeV, at an incidence angle of 140°. The data were analyzed with the standard code Ion Beam Analysis (IBA) Nuno's Data Furnace (NDF) [40]. Photoluminescence (PL) measurements were performed using a 355 nm excitation wavelength at a nominal power of 1 mW from a CW optically-pumped semiconductor laser (Coherent Genesis CX STM-Series), and with a 455 nm laser (EKSMA EO-50%-NL50) (see supplementary material). The light emitted by the films was collected with a Czerny-Turner type Monochromator (Acton Spectra Pro300i, with a diffraction grating of 1200 g/mm for the visible range) and detected through a photomultiplier (EMI 9659QB-S20), the signal was amplified with the standard lock-in technique and collected by a CPU. All the PL spectra were measured at room temperature and they were corrected by the spectral response of the optical system using a calibrated lamp. The photoluminescence excitation spectra (PLE), was recorded using a FluoroMax-4 spectrofluorometer (Horiba Jobin Yvon) in the 400–800 nm range for the emission, and in the 200–500 nm range to fully characterize the excitation.

2. Results

2.1. Film composition

Reference SiAlON thin films have a composition of Si* (37.7%) - O (19.3%) - N (37.2%) - ca + Y (5.8%), where Si* takes into account the contribution of Al + Si, since RBS cannot resolve the overlap of these elements in the acquired spectra [33]. However, in samples deposited under the same conditions and using the same target, the aluminum content was found to be approximately 3% by means of XPS [39]. The incorporation of the Eu in the films, although is in doping levels of a few percent, leads to a modification on the relative composition of the films, as it is shown in Fig. 1(a) and 1(b). The analysis of the results shows that the Eu content increases linearly with the number of ablation pulses on the europium target used for doping, resulting in a Eu content of 1.4%, 2.8% and 5.6%, for the films prepared with 10, 20 and 40 pulses of Eu, respectively. Concerning to the film composition, while the N to Si* ratio remains steady as a function of the number of Eu pulses, as can be seen in Fig. 1(b), however there is a significant increment of the ratio of O to Si*, especially in the 40 pulses sample. Because it is known that the europium tends to oxidize easily [41,42], since it has a large affinity for oxygen this might explain the increase of oxygen content in the films when more Eu is introduced.

In order to determine the oxidation state of the incorporated ions we performed XPS analysis. In Fig. 2 we show the part of the spectrum corresponding to the Eu 3d signal for the film doped with 40 Eu pulses (5.6% Eu). In Fig. 2(a) it is shown the intensity of the Eu 3d peaks as a function of the depth in the film. After the thermal annealing treatments, it is found that most of the Eu is distributed in the central region of the film and at the surface there is no Eu doping, corresponding to the capping layer of 25 nm. In Fig. 2(b) it is shown the spectrum of the 3d Eu region taken at the centre of the film (≈80 nm). The plot shows the characteristic peaks at 1127 and 1157 eV corresponding to the Eu^{2+} oxidation state and the individual smaller peak corresponding to the satellite signal in 1135 eV [43,44]. There are no peaks corresponding to the Eu^{3+} oxidation state. This result indicates that the Eu ions in our films have remained in the Eu^{2+} oxidation state, even after the annealing treatments, demonstrating the excellent qualities of the SiAlON matrices as antioxidants for europium doping. This effect might also be attributed to the aluminum content present in the SiAlON host, as due to the GFE (Gibbs formation energy) of Al_2O_3 and Eu_2O_3 (Eu^{3+}), −1582 and −1565 kJ·mol^{-1}, respectively, and the oxygen loss process attributed to the kinetics of the ablation plume. Therefore, the remaining oxygen would be forming Al_2O_3 instead of Eu_2O_3 [28].

2.2. Linear optical properties. Ellipsometry

In Fig. 3 can be seen the evolution of the complex refractive index $\mathbf{n} = n + ik$, the refractive index n and of the extinction coefficient k values, as a function of wavelength, for samples after the annealing at 700 °C that was performed to improve the Eu^{2+} light emission [33]. The n

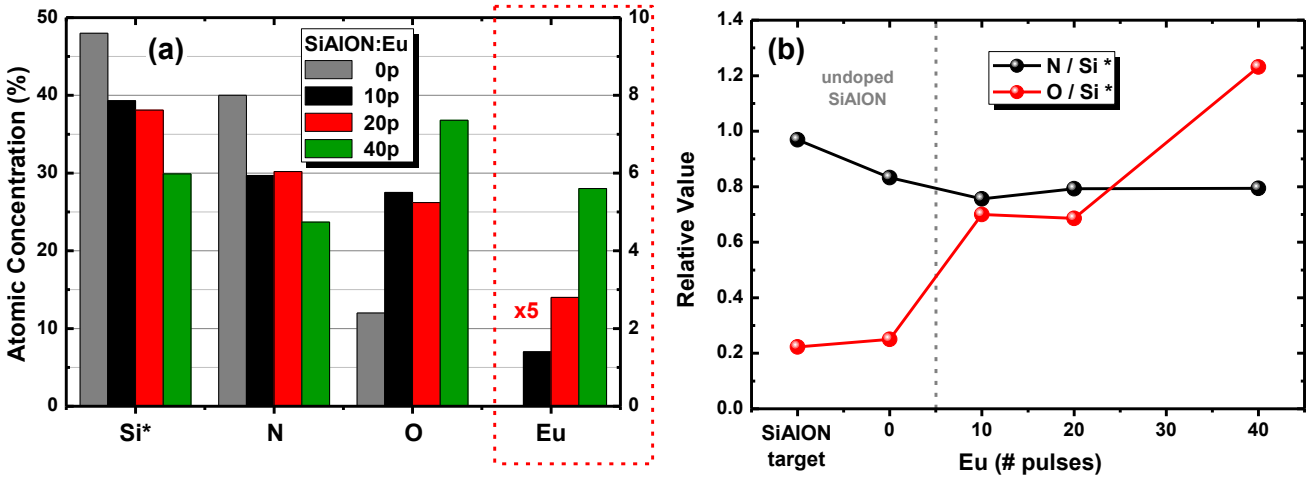

Fig. 1. (a) Atomic concentration obtained by RBS analysis (NOTE: the right axis has been amplified x5 for visual aid of the Eu composition), (b) Relative composition of N and O to Si*. The masurements correspond to the Eu-doped film with 40 pulses.

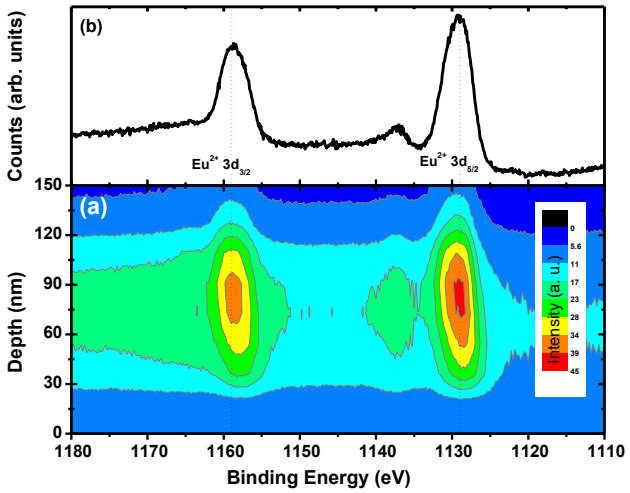

Fig. 2. XPS results of the 5.6 at.% Eu-doped SiAlON thin films after the annealing at 700 °C. (a) Spectra of the 3d Eu signal as a function of the film depth (b) Spectrum of the Eu3d region at ≈80 nm penetration.

values of the undoped films are higher than that of the Eu-doped films, Fig. 3(a), for samples doped with 1.4 and 2.8 at. %Eu were very similar, however the films with 5.6 at. % Eu exhibited a considerable decrease in the *n* values over the entire wavelength ($\Delta n \approx 0.15$ at 620 nm, Fig. 3(b)). This result is in good agreement with the fact that by RBS it was observed that the oxygen content increased considerably, thus, we can conclude that the increase of oxidation of the films results in a decrease in the refractive index. The extinction coefficient was low for all the films, below our detection limit (10^{-3}) in the visible and near infrared region of the spectrum. Therefore, the films show an excellent transparency in the studied spectral region. This is an important result, because it demonstrates once again that SIAlON is an excellent matrix to incorporate active materials to achieve a simultaneous VIS-NIR-IR emission using different dopants. Indeed, we have demonstrated the optical performance of IR emission in Erbium doped SIAlON thin films [32].

2.3. Optical performance. Emission

In order to obtain the photoluminescence excitation spectra (PLE) of the Eu-doped films, it was monitoring the wavelength at which the photoluminescence (PL) was maximum in each case, the results are

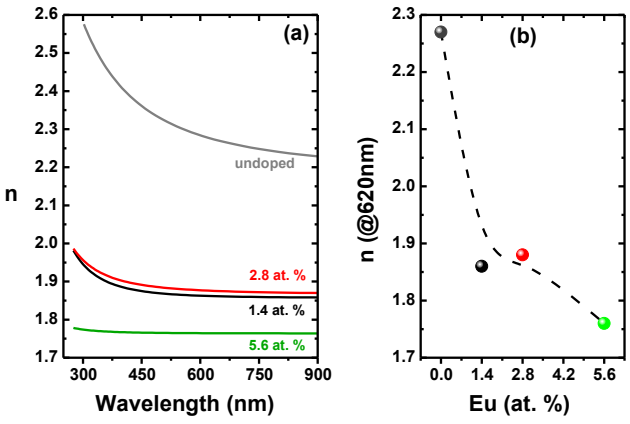

Fig. 3. (a) Refractive index **n** of the Eu-doped films, (b) **n** value for undoped and Eu-doped films at 620 nm.

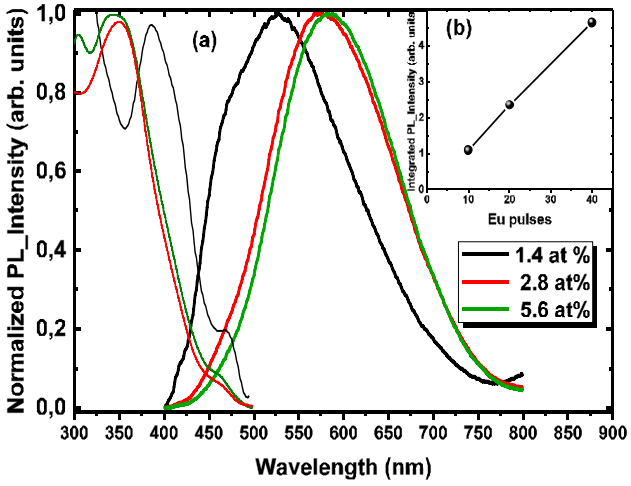

Fig. 4. Photoluminescence spectra of excitation (PLE) and emission (PL), of the SiAlON:Eu^{2+} films . The inset shows the increase of the integrated PL Intensity spectra of the samples at the highest emission, which was after annealing at 700 °C.

shown in Fig. 4 on the left side. The PLE shows a band of about 50 nm FWHM in the 300–400 nm spectral region that emerges from the absorption from the ground state to the of the $^4f_6^5d_1 \rightarrow {}^8S_{7/2}$ optical transition level. The corresponding photoluminescence spectra PL are shown on the right side of Fig. 4. They were obtained by excitation with 355 nm and they show very wide bands of about 210–270 nm FWHM covering the whole visible region from 400 to 800 nm corresponding to the sole transition of the degenerated Eu^{2+}:$^4f_6^5d_1$ level to the ground state $^8S_{7/2}$. The spectral width of these spectra is wider than those previously reported [33], for films doped with Eu that have shown FWHM of 140–200 nm to 200–220 nm. The reason of this wide-band emission might be attributed to the amorphous structure of the SiAlON thin films after the annealing treatments. Indeed, the 5d orbitals of Eu^{2+} ions are extremely sensitive to changes in the surroundings, due to its position in the outer shell, compared to 4f orbitals [26]. This means that, as we incorporate oxygen and europium into the SiAlON host, oxygen preferably forms Al_2O_3, maintaining the 2+ oxidation state of europium. This effect therefore causes stoichiometric changes in the SiAlON host matrix, thus directly affecting the energy of the 5d orbitals of the Eu^{2+} ions, which are very sensitive to the local environment. This is due to the so called nephelauxetic effect, which is related to anion polarizability, electronegativity of the ions, and dopant-bond distances, and the crystal field splitting, which is influenced by the nature and the coordination number of the dopant ion as well as the arrangement and the nature of the atomic bonds [45]. As a result of the variation of the position of the 5d levels energy position the photoluminescence emission is tuned. In addition, the amorphous phase of our films is a non-ordered structure which affects differently to the configuration of the 5d orbitals allowing for the broadening of the emission [46].

It was observed that the PL intensity increases and its spectral distribution shifts towards higher wavelengths as the Eu concentration increases; and as seen previously [33], there is also a shift to smaller wavelengths during the annealing treatments up to 700 °C. At this point it is noteworthy that none of the studied films exhibited narrow emissions characteristic of Eu^{3+}, known as the f-f transitions, which is consistent with the XPS results that show only the presence of Eu^{2+} in our films.

In order to study possibility of exciting the SiAlON:Eu^{2+} films by UV pumping in the near UV (380–420 nm) we have studied the emission spectra under excitation at 405 nm. The results are shown in supplementary material S1. The results how that indeed the Eu-doped films can be efficiently excited at 405 nm and the resulting PLE spectra show the same basic features, i.e. peak maxima position and spectral width than those excited at 355 nm.

In order to assess the spectral distribution in the visible region of these broadband emissions, the spectra obtained for the films were analyzed using the three-color matching functions established by the Commission Internationale de l'Éclairage (CIE) in 1931, known as the CIE 1931 x-y color matching functions. The chromaticity diagram in Fig. 5 indicates the chromatic coordinates corresponding the Eu-doped SiAlON thin films; furthermore, by means of the McCamy formula [47] we were able to associate the CIE coordinates of the emissions with the Correlated Color Temperature (CCT). The sample with 10 pulses (1.4 at. % Eu) exhibited a green emission, which corresponds to a CCT of 5965 K; whilst the samples with 20 and 40 pulses (2.8 and 5.6 at. % Eu, respectively) showed yellow emissions equivalent to CCTs of 3477 and 3130 K, respectively. In Table 1 we present the CIE coordinates and its associated CCTs. The results show the potential of europium doped SIAlON thanks to the high visible broad emissions shown by these films up to 270 nm that could make them extremely valuable for integrated devices as phosphors nano-emitters in white-light LEDs.

3. Conclusions

We show the excellent properties of Eu-doped SiAlON nanostructured thin films produced by means of the alternate laser ablation of independent SiAlON and Eu targets. The results show that we were able to nanostructure these films in a multilayer system in which the local Eu concentration was varied. The compositional analyses show that the increase of content of O in the films is associated with the increase of Eu doping, in turn this results in a decrease of refractive index of the films respect to the undoped films. The films show that the Eu ions are incorporated in the reduced 2+ oxidation state, that is well preserved after the annealing treatments, demonstrating the excellent qualities of the SiAlON matrices as antioxidants for europium doping. The optical properties show intermediate refractive index values between that of silicon nitride and silicon oxide, and with a tendency to decrease upon Eu doping and subsequent thermal annealing. Under excitation, the films exhibit intense PL emission in the visible range with an extremely broad band of FWHM >210 nm associated to the successful Eu^{2+} nanostructured doping. Moreover, with the increase in Eu^{2+} concentration the color of the emitted light changes from bluish to orange, which is explained as a result of the change of the local environment around the Eu^{2+} ions. These results are encouraging in the path to achieve tunable emission with a single dopant rare-earth ion, and point out oxynitride films as a promising platform for the design of active nano-emitters with color control in LED devices.

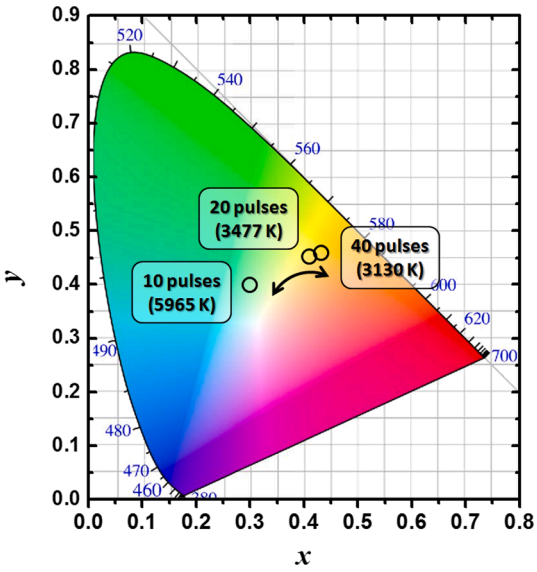

Fig. 5. CIE 1931 chromaticity diagram of the Eu-doped SiAlON films after the 700 °C annealing.

Table 1
CIE coordinates and CCTs calculated with McCamy formula, for the Eu-doped SiAlON thin films after the 700 °C annealing.

Sample (Eu pulses)	*x*	*y*	CCT (K)
10	0.31779	0.41094	5965
20	0.43234	0.46052	3477
40	0.45782	0.46662	3130

Contribution statement

I.C. and A.M-J carried out the experiments, sample preparation and characterization. I.C. wrote the original manuscript with support from AM-J and R.S. And RS conceived the original idea and supervised the project, including the final writing-reviewing and editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2022.156037.

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