Electrochemical Modification of the Optical and Electrical Properties of Cd-rich $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ alloys

Mimoza M. Ristova^{*a,b}, Christopher Francis^{a,c}, Francesca Toma^c, Kin M. Yu^{a,d} and Wladislaw Walukiewicz^a

^aLawrence Berkeley National Laboratory, Materials Sciences Division, Berkeley, California 94720, USA

^b Physics ^bDepartment, Faculty of Natural Sciences and Mathematics, University Ss Cyril and Methodius, Arhimedova 10, 1000 Skopje, Republic of Macedonia

^cLawrence Berkeley National Laboratory, JCAP, Berkeley, California 94720, USA

^dDepartment of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong

Abstract

Enhancement of the optical and electrical properties of Cd-rich $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ alloys was achieved through an electrochemical procedure – their biasing at a constant negative potential into an electrolyte. Depending on film's conductivity (correlated to x), the films changed their color from transparent-yellowish to black. For a certain bias, the coloration became permanent and irreversible. Electron concentration for some samples increased for better than two orders of magnitude upon the coloration, while as the mobility decreased for a factor of 2 to 10. Rutherford Back Scattering (RBS) analysis revealed oxygen deficiency for the colored samples. The XRD analysis showed that the coloration could be associated to a partial reduction of CdO_2 to CdO . XPS analysis suggested complex red-ox transitions of the two Ni and two Cd-oxides within the alloy. $\text{Ni}2p$ electrons suggested that a partial NiO (transparent) transition to Ni_2O_3 (black) could be responsible for the occurrence of the intensive light trapping. Since the $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ band gap is tunable with x , one may conclude that this electrochemical procedure is motivating for tuning/modification/enhancement of the both, the absorption and conductivity of $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ films for their possible application as single film photoanodes (TCO and PEC cell in one) within a hybrid water splitting device.

1. Introduction

There has been a renewed interest in CdO -based materials for transparent conductor applications due to their outstanding electron mobility, and visible and infrared (VIS and IR) transparency [1-5]. Cadmium oxide (CdO) belongs to a category of the semiconductor

metal oxides, which is widely used for various scientific and industrial fields because of its convenient catalytic, optical, and electrical properties. CdO is an n-type semiconductor with an intrinsic direct gap at 2.2 - 2.5 eV [6], respectable transparency, and near metallic conductivity. CdO has been considered as a prospective TCO material. Doping of the CdO with certain dopants, such as Zn [7] or Mg [8] results into widening the band gap to higher values than 2.2 eV, creating a complex light absorption model that includes the both, direct and indirect transitions. NiO, on the other hand, is a well-known p-type semiconductor with a wide direct band gap of 3.7 eV. It also reveals electrochromic properties, providing a dynamical control of the transmitted light [9]. NiO has been applied in electrochromic technologies [10-14]. The transmittance switching (coloration and bleaching) of the NiO material is known to result from the reversible redox conversion of nickel oxide (colorless) into nickel hydroxide (black in color), $\text{NiO} \leftrightarrow \text{NiOOH}$ [15]. Doping/alloying the CdO with Ni/NiO has been examined by means of $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ compound across the entire alloying region [16]. The authors from Ref. 16 found that the intrinsic band gap (E_g) of the alloys can be tuned continuously from 2.2 eV (CdO) to 3.63 eV (NiO) with increasing the Ni-content, using the bowing equation with 1.26 for the bowing factor. The aim of this research was to examine the possibility of modifying the optical and electrical properties of Cd-rich $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ material, which appeared to be highly conductive and highly absorptive for photon energies greater than 2 eV. This research revealed that the electrochemical reduction of $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ films results into an irreversible and controllable modification of the optical and electrical properties. The band offset diagrams of metal oxides that have been considered in the literature for water splitting are given on Fig. 1. It has been reported that the Valence Band Maximum (VBM) of CdO moves up for about 1 eV relative to the vacuum level as the Ni-content increases from 0 and 0.35 [16] while as the Conduction Band Minimum (CBM) remains almost the same. This VBM change is depicted as a purple striped block on the top of the CdO-VBM on Fig. 1. Hence, one could assume that a supplementary potential shift “upwards” could level up the VBM and CBM to a favorable position with respect to the water splitting potentials, $\phi(\text{H}^+/\text{H}_2)$ and $\phi(\text{O}_2/\text{H}_2\text{O})$.

2. Experimental

Nominally, near stoichiometrical $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ films were grown on glass substrates, using dual gun radio frequency (RF) magnetron sputtering system with two separate targets, NiO and CdO, both of 99.9% purity. The sputtering conditions of $\text{Cd}_x\text{Ni}_{1-x}\text{O}$ films have been reported elsewhere [16]: the chamber was initially evacuated to 1×10^{-6} Torr prior to deposition; the background pressure was maintained at 5 mTorr of Ar-gas; the substrate temperature was 270 °C; the RF power of the CdO target was 100 W, whereas the target-to-substrate distance was 4 cm for all samples. Different Ni-contents ($0 < x < 0.35$) in the $\text{Cd}_x\text{Ni}_{1-x}\text{O}$ were achieved by varying the RF power of the NiO target from 20 to 120 W at a target-to-substrate distance of 3.5 cm. The contents of Ni (x), Cd and O were evaluated by

Rutherford backscattering spectrometry (RBS), using a 3.04 MeV He⁺⁺ beam. The RBS spectra were also used for film thickness (*t*) calculations. The crystal structure of the films was analyzed by x-ray diffraction (XRD) using Cu K- α radiation. Scanning electron Microscopy (SEM) images and Energy Dispersion X-ray spectra (EDX) were taken by HITACHI 4300 SE/N SEM equipped with Thermo EDX system. Optical spectroscopy measurements (reflectance and transmittance) were made over the photon wavelength range from 240 to 2400 nm, using Perkin-Elmer URA Spectrophotometer. Electrical properties of the films, including electron concentration and mobility, were obtained from the Hall-effect measurements, using a van der Pauw configuration with a magnetic field of 0.6 T at room temperature. Electrochemical coloration of the films was achievable only with Cd-rich samples ($x < 0.3$) because of their high conductivity [16], which is crucial for the injected charges to be able to reduce the film at the interface with the electrolyte. Electrochemical treatment was performed into 0.1 M dipotassium phosphate (K₂HPO₄) in which the Cd_{*x*}Ni_{1-*x*}O films on glass were employed as working electrodes. Gamry Reference 600 Potentiostat was used for biasing the films at a constant voltage. Application of the negative bias (reduction) on the Cd_{*x*}Ni_{1-*x*}O film against the Pt-electrode invoked coloration of the Cd_{*x*}Ni_{1-*x*}O films, turning film's color from transparent-yellowish into black color tones. The colored Cd_{*x*}Ni_{1-*x*}O films were further electrochemically treated with inverse (positive) potential, in expectation to invoke opposite reaction - oxidation, i. e. to bleach the samples.

3. Results and discussion

The following Ni_{*x*}Cd_{1-*x*}O samples with different Ni-contents and thicknesses were synthesized for this study: R333 ($x=0.35$, $t=244$ nm); R334 ($x=0.29$, $t=160$ nm); R335 ($x=0.24$, $t=160$ nm); R336 ($x=0.16$, $t=134$ nm); R338 ($x=0.03$, $t=110$ nm) and R734 ($x=0.21$, $t=160$ nm). The intriguing experiment was initially performed on R335 (Ni_{0.24}Cd_{0.76}O) as-grown film. Fractions of the same sample were biased at potentials -1.5 V and -3 V against Pt-electrode into the electrolyte. The duration of the applied bias was determined by the time after which the current achieved saturation. The experiment was also performed with pure CdO sample (containing no Ni): the coloration phenomenon wasn't observed. This suggested that Ni-oxide compounds must be responsible for the film's coloration effect. Fig. 2 shows (a) photographs of the Ni_{0.24}Cd_{0.76}O films in their as-grown, colored and bleached states against a white background, depicting the change of the film's color upon the electrochemical treatment under different potentials, and (b) modification of the VIS and NIR transmittance spectra of the same films from (a). From Fig. 2(b) it is obvious that the film colored at -3 V (black line) is apparently darker than that at -1.5 V (gray line). Furthermore, one could see that the positive potentials (+1.5 V, +3 V) didn't induce any visible bleaching of the samples (compare the purple, red and orange lines), as expected from the analogy with the reversible electrochromic NiO into NiOOH

turnover (transparent to black and reverse) [9]. Furthermore, the colored films at negative potentials were then, positively biased in the electrolyte, in order to examine an eventual reversibility of the coloration process. Nevertheless, the transmittance spectra on Fig. 2(b) showed that the colored films which were previously biased with -1.5 V were partly brought back to a transparent state when biased with +1.5 V (compare gray and blue lines). Furthermore, the colored films with -3 V didn't regain their transparency after being treated with +3 V (compare black and green lines). Hence, the inverse biasing apparently didn't provide full reversibility, suggesting that the acquired electrochemical coloration was irreversible and remained as a permanent state of the film.

Further examinations were made with another as-grown R338 ($\text{Ni}_{0.03}\text{Cd}_{0.97}\text{O}$) sample. The fragments from the same film were biased under different negative voltages, ranging from 0 to -4 V. The time of coloration of each film was determined by the time after which the current roughly stabilized, although at higher biases it never fully stabilized because the obvious corrosion. Nevertheless, the films changed their color into different color grades, from gray-yellowish to black. The transmittance spectra of the colored films are given on Fig. 3. The inset in the figure presents the transmittance change at 550 nm (solar maximum) on the applied bias. One could see that the transparency abruptly changed at biases greater than -2 V, suggesting that the electrochemical reaction revealed a voltage threshold at about -2 V. Our further tests made it clear that the coloration process was independent of the quantity of the injected/ejected charges ($Q=It$). Different coloration levels were achieved at different potentials even though the charge quantity (Q), remained constant.

The as-grown and the colored $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ films were characterized by RBS. The results for one representing R335 sample ($\text{Ni}_{0.16}\text{Cd}_{0.84}\text{O}$) are given on Fig. 4. The RUMP software for nuclear interactions simulation showed that the electrochemical coloration process induced oxygen deficiency, which is obvious from the relative drop of the oxygen peak, as shown on Fig. 4.

XPS spectra were recorded from the untreated surfaces of several $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ films. However, we present the analysis made on Cd3d, 2pNi and O1s XPS spectra, taken from the R734 ($\text{Ni}_{0.21}\text{Cd}_{0.79}\text{O}$) sample, as-grown and colored at -2 V. Fig. 5 presents: (a) Cd3d, (b) Ni2p and (c) O1s comparative spectra. The XPS multiplex spectra of the Cd 3d_{5/2} and 3d_{3/2} peaks from the as-grown and colored films are shown in Fig. 5(a). Obviously, the Cd 3d_{5/2} and 3d_{3/2} peaks are symmetric and centrally located at 404.2 eV and 411.0 eV. The difference between these peaks is 6.8 eV, which is in good agreement with the 6.74 eV spin-orbit energy splitting between Cd 3d_{5/2} and 3d_{3/2} states [17]. Deconvolution of the Cd 3d_{5/2} peak renders two Gaussian peaks with binding energies 405.0 eV and 403.6 eV. These binding states could be associated with CdO and Cd(OH)₂/CdO₂, respectively [18], suggesting a mixed phase nature of the as-grown $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ alloys. Having in mind the

hydrogenless RF film growing procedure, the presence of $\text{Cd}(\text{OH})_2$ should be ruled out. Moreover, the change in the Gaussian areas of the 3dCd peaks indicated a change in the contribution of each oxide phase, following the electrochemical coloration at -2 V. It could be also noted that upon the coloration, a portion of the Cd-peroxide (CdO_2) was reduced to Cd-oxide (CdO) since the peak area pertaining to CdO_2 relatively decreased with respect to the one of CdO . The latter suggests that the concerning chemical conversion due to the coloration process increases the concentration of oxygen vacancies in the “nominally” stoichiometric compound. Figure 5(b) shows the $2p\text{Ni}_{1/2}$ and $2p\text{Ni}_{3/2}$ XPS multiple peaks of the as-grown and colored $\text{Ni}_{0.21}\text{Cd}_{0.79}\text{O}$ film. The results suggested a presence of a mixed Ni-oxide phase: NiO , Ni_2O_3 and $\text{Ni}(\text{OH})_2$. Again, the likelihood for the presence of the hydroxide compound was negligible due to the controlled absence of hydrogen during the RF sputtering process. The deconvolution of the $2p\text{Ni}_{3/2}$ rendered two Gaussian peaks, 854.3 eV and 855.9 eV. These could be assigned to NiO (855.0 eV [9]) and Ni_2O_3 (856 eV [19]) respectively. The possibility for the presence of elemental Ni contribution with a low-intensity peak at 852.5 eV [19] could not be ruled out. One may also notice that the Ni_2O_3 content increased due to the coloration procedure. The increase of the black in the color Ni_2O_3 compound is probably responsible for the coloration process and, therefore, the decrease in the transparency. This observation seems like an unusual complex electrochemical red-ox reaction in which, under the same cathodic bias the Cd-peroxide gets partly reduced, while as the NiO gets partly oxidized. One should also bear in mind that CdO_2 and Ni_2O_3 are not well-examined semiconductors. Figure 5(c) shows the $\text{O}1s$ XPS spectrum of the film in its as-grown and colored states. The fitted Gaussian peaks from Fig. 5(c) are positioned as follows: 531.2 eV, 533.2 eV, 530.9 eV and 528.3 eV, which is in good agreement with the literature. The literature values of the four oxide phases CdO , CdO_2 , Ni_2O_3 and NiO fall around: 528.4 eV, 531.1 eV, 531.7 eV and 533.5 eV [18-21] respectively. Furthermore, as evident from Fig. 5(c) that the coloration of the $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ is followed with a decrease of $\text{O}1s$ electrons associated to NiO due to their phase transition into Ni_2O_3 . These results are consistent with the findings from Fig. 5(b). Also, the coloration is obviously followed by a transition of $\text{O}1s$ electrons originating from CdO_2 to CdO , which is in a good agreement with the conclusions derived from Fig. 5 (a). Nonetheless, this complex, multi-compound electrochemical redox process involving minimum four oxides, remains to be studied in the future.

Figure 6 shows the XRD patterns of two representing $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ films with different Ni-contents ($x=0.03$ and 0.16) in their as-grown and colored states. The few detectable diffraction maxima could be related solely to Cd-oxide polycrystalline phases. Ni-O phases were, for both films, however, below the detection limit. According to the XRD patterns on Fig. 6, the as-deposited and the colored films consisted of both crystalline and amorphous phases, which is evident from the diffraction peaks and the amorphous hump within the 2 Theta range from 20 to 35° . Furthermore, it is evident that the crystalline phase of the as-

grown films consisted mainly from cubic CdO [22], with energetically preferred orientation along the (200) plane and a cubic CdO₂, occurring as a (222) peak [23]. Similar amorpho-polycrystalline XRD-pattern of CdO films doped with Ni has been reported by other authors, who examined films prepared by sol-gel [24]. Furthermore, similar films prepared by vacuum evaporation appeared to be fully polycrystalline with energetically preferred orientation along the (111) plane [25]. The patterns from Fig. 6 also suggested that the film coloration induced partial oxide phase transition from cubic CdO₂ into cubic CdO, with energetically preferred orientation along the (111) plane. Unfortunately, the patterns didn't yield any information, nor for a presence of elemental Cd, neither for the Ni-oxide phase transformation due to the coloration procedure. The conclusions derived from the XRD results, regarding the CdO₂ into CdO transition due to coloration, matched those from the XPS measurements.

The SEM images from Fig. 7 were taken from the film R336 (Ni_{0.16}Cd_{0.84}O) in it's: (a) as-deposited, and (b) colored state achieved at -2V. Both the micrograms reveal surfaces of granular morphology with rather compact structure – densely packed round grains 200-400 nm in diameter with poor porosity. No particular difference could be reported from comparing the two SEMs. Hence, the electrochemical coloration does not induce any notable changes on the surface morphology of the films. Furthermore, the EDX spectra on Fig. 7(c) were taken from the as-prepared film, as well as from the FTO substrate. Using the spectral peak areas of Ni peak at 7.5 eV (591 a.u.) and Cd peak at 3.2 keV (3302 a.u.), the Cd/Ni ratio was calculated to be 5.59. For comparison, the Ni/Cd ratio established from RBS was Cd/Ni=0.84/0.16 = 5.25. This difference could be ascribed to the relatively higher noise with respect to the signal for the EDX peak of Ni at 7.5 eV.

The absorption coefficient (α) was evaluated from the Beer-Lambert's law, using the transmittance spectra (T %) as shown on Fig. 8(a), reflectance spectra (R %) from Fig. 8(b), and the film's thickness calculated from all the RBS measurements. One may see that the both sets of spectra (T % and R %) show interference maxima and minima. The optical absorption coefficient (α) spectra for these films are shown on Fig. 8(c). The absorption edge, E_{AE} , was obtained by linear extrapolation of the α^2 plots from Fig. 9 to their corresponding baselines [24]. Values of the absorption edge, determined graphically, are not necessarily the intrinsic band gaps of the materials because of the high electron concentrations of CdO compounds [16]. From Fig. 9 it is evident that the indirect transitions became more pronounced upon the coloration. Furthermore, the evaluated absorption edges for the both, as-grown and electrochemically colored samples generally matched. As shown on Fig. 9, the absorption edges of samples with $x=0.03$; $x=0.16$; $x=0.24$ and $x=0.35$ ranged from 2.6 eV to 2.9 eV for the both sets of films (as-grown and electrochemically colored). These values are in good agreement with experimental results

presented by C. Francis *et al.* [16] and F. Yakuphanoglu [24] (for the film with $x=0.03$). Obviously, the absorption edges were not affected by the electrocoloration process.

Fig. 10 summarizes the measured electrical properties of the concerned alloys that exhibited n-type conductivity. As could be seen from Fig. 10(a), the electron concentration for all the three sets of films, the as-grown, bleached and colored, grew with the decrease of Ni content (x). However, it is evident that the electron concentration of the colored $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ films became near metallic ($\sim 10^{22} \text{ cm}^{-3}$). Moreover, it is evident that the electrochemical coloration pumped up the conduction band with considerable supplemental quantities of electrons, observed throughout the entire region of interest ($x < 0.3$). The electron mobility, as evident from Fig. 10(b), underwent respectable reduction upon the electrochemical coloration. The decrease was, however, most pronounced for the Cd-rich samples. The bleaching, on the other side, provoked a small mobility increase. For instance, for $\text{Ni}_{0.03}\text{Cd}_{0.97}\text{O}$ film the mobility upon bleaching at +3 V increased from $71 \text{ cm}^2/\text{Vs}$ to $82 \text{ cm}^2/\text{Vs}$. Similar result as for the bleached state has been reported by other authors of as-deposited CdO doped with 3-4% Ni [25]. However, it is evident that the electrochemical coloration induced drastic drop of the electron mobility to about $3\text{-}8 \text{ cm}^2/\text{Vs}$, depending on the Ni-content. However, the overall conductivity grew upon the coloration since the mobility fall is prevailed by the electron concentration growth. For instance, for $\text{Ni}_{0.03}\text{Cd}_{0.97}\text{O}$ the electron conductivity increased from 4×10^3 to $18 \times 10^3 \text{ }\Omega\text{cm}$ upon coloration. The increase in electron concentration with the Cd-content has been explained elsewhere by the large conduction band offset of 4.4 eV between CdO and NiO [16]. However, the growth in conductivity upon electrochemical coloration becomes more pronounced for the samples with small Ni-contents (small x). Hence, one may conclude that the level of the coloration (the increase of the absorbance) could be related to the film's initial conductivity: Cd-rich samples are more conductive and thus get darker upon coloration. On the other side, the coloration is strictly determined by the presence of the NiO compound: even tinny amounts of Ni ($x < 0.03$) produce completely black (non-transparent films). The overall complex phenomenology of enhanced light absorbance and conductivity due to coloration could thus be tentatively explained with the oxygen deficiency (oxide vacancies) that occur in $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ alloy (proved by RBS and XRD), but also with the internal oxygen redistribution among the oxide phases (proved by XPS). In other word, the electrochemical coloration reaction invokes internal redox exchange among the minimum four oxide compounds on the solid-liquid interface (CdO, CdO_2 , NiO, and Ni_2O_3). Hence, the extraordinary intensive changes in the film transparency are probably assisted by the higher electron concentrations of the Cd-rich samples, allowing the irreversible electrochemical transformations of small portions of NiO (transparent) into Ni_2O_3 (black) to take place. The dramatic growth in the conductivity of the colored films could be ascribed to the increased concentration of donor levels, probably resulting from the oxygen vacancies that occur in the CdO_2 compound due to its transformation into CdO. These levels

may also exhibit strong interaction with the localized d-states of Ni and the conduction band [16].

4. Conclusion

Voltage-dependent irreversible coloration was observed upon electrochemical reduction of RF sputtered $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ films for $x < 0.3$. The VIS and NIR light absorption and conductivity of the films were controllably modified due to a prescribed electrochemical process. The RBS, XRD, and XPS analysis showed that the electrochemical coloration of the $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ films was accomplished by a complex redox process: partial reduction of CdO_2 into CdO and simultaneous partial oxidation of NiO to Ni_2O_3 . The both CdO_2 and Ni_2O_3 are, however, less examined semiconductors, and this unusual behavior needs to be clarified with other analytical experiments. However, NiO transition to Ni_2O_3 (black in color) appears to be probably the only responsible mechanism for the drastic increase of the absorption (coloration), i.e. the intensive light trapping mechanism. However, the background of the electron conductivity increase is not straight forward. It could be tentatively ascribed to donor levels originating from the oxygen vacancies within the CdO_2 compound and their interaction with the Ni *d*-states and the conduction band. These assumptions remain to be confirmed in the future. From all the presented above, it follows that the optical and electrical properties of the as-grown $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ films, besides being tunable during the synthesis with the Ni-content (x), they could be further tuned with the proposed supplementary electrochemical reduction. Having in mind that the $\text{Ni}_x\text{Cd}_{1-x}\text{O}$'s band gap could be tuned by varying the Ni-content (the valence band maximum moves to higher values relative to the vacuum), one may conclude that the proposed electrochemical procedure is motivating for further tuning/modification/enhancement of the absorption and conductivity of $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ films for their possible application as single film photoanodes within a hybrid water splitting device (TCO and PEC cell in one).

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Captions to the figures

Fig. 1. Band offset diagram of selected oxide materials, considered for water splitting. The purple stripped block on the top of the VBM of CdO pertains to the VB shift upwards as a function of Ni-content raise from 0 to 0.35. Water splitting potentials, $\phi(\text{H}^+/\text{H}_2)$ and $\phi(\text{O}_2/\text{H}_2\text{O})$, as well as the Fermi stabilization level (E_{FS}) are presented.

Fig. 2. (a) Photograph of $\text{Ni}_{0.24}\text{Cd}_{0.76}\text{O}$ film against a white background under white light in its as-grown state, bleached state at +3 V, colored at -1.5 V, colored and then bleached with +1.5 V, colored at -3 V, colored and then bleached with +3V; (b) Transmittance spectra of the films from (a).

Fig. 3. Visible transmittance spectra from $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ ($x=0.03$) colored under different potentials (from 0 to -4 V). Near equal charge (Q) was used for the reduction (coloration) of all films.

Fig. 4. RBS of $\text{Ni}_{0.16}\text{Cd}_{0.84}\text{O}$ in its as-grown and colored states. The peaks pertain to Cd, Ni and O.

Fig. 5. XPS spectra of: (a) Cd3d electrons; (b) Ni2p –electrons; (c) O1s electrons of $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ films in their as-grown and colored states.

Fig. 6. XRD patterns of $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ films ($x=0.03$ and 0.16) in their as-grown and colored states.

Fig. 7. SEM/EDX analysis on $\text{Ni}_{0.16}\text{O}_{0.84}\text{O}$ film on FTO substrate: (a) SEM of the surface of as-prepared; and (b) colored state; (c) EDX spectrum taken for the as prepared film (EDX of FTO substrate is given for comparison).

Fig. 8. (a) Transmittance spectra; (b) reflectance spectra; (c) absorption coefficient spectra for four Cd-rich samples in their as-grown and colored states.

Fig. 9. α^2 versus $h\nu$ presentation: (a) as-grown $\text{Ni}_x\text{Cd}_{1-x}\text{O}$ films ($x=0.03$; 0.16; 0.24 and 0.35); (b) colored with -3 V. The optical absorption edges (E_{AE}) were evaluated by extrapolation of the linear part of $\alpha^2 = f(h\nu)$ to corresponding baselines.

Fig. 10. Electrical properties of Cd-rich samples in their as-grown and colored state: (a) electron concentration; (b) electron mobility.

Figure 1

(b)

Figure 2.

Figure 3.

Figure 4

Figure 5(a)

Figure 5(b)

Figure 5(c)

Figure 6.

Figure 7

Figure 7(c)

Figure 8(a)

Figure 8(b)

Figure 8(c)

Figure 9(a)

Figure 9(b)

Figure 10(a)

Figure 10(b)