

Electrolytically deposited Cadmium Selenide Films for Photovoltaic Applications

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Abstract. CdSe films were electrodeposited on pure nickel substrates. The nickel substrate was polished to a mirror finish by Al₂O₃ paste, etched in 10% HCl solution for 40 s and rinsed thoroughly by de-ionized water. The deposition bath contained solutions with excessive Cd²⁺ (0.2M) from CdSO₄ and small amounts of SeO₂ (1x10⁻³ M). The pH of the bath was adjusted to a value of 2.2 at RT by adding 10% H₂SO₄. The bath was first thermostated at the required temperature, which varied from 55°C to 65°C. Plating was accomplished at deposition potential 1000 mV (vs. Hg/Hg₂SO₄). The films formed had a uniform thickness and it was found to be approximately 2.0 μm thick (for 20 min electrodeposition process). The produced CdSe films were characterized by X-Ray diffraction and SEM. The induced semiconductor doping effect by thermal annealing in pure dry nitrogen gas was also investigated. Gold contacts were placed on top of the CdSe films, either by evaporation, or mechanically. Depending on the deposition parameters the electrical characteristics of the Ni/CdSe/Au structures may exhibit rectification properties. The optical excitation of the structure was investigated for various CdSe thicknesses.

1 Introduction

Cadmium selenide (CdSe) is a well-known II-VI semiconductor, crystallizing in either the wurtzite (hexagonal structure), or the zinc blende (cubic structure). The cubic structure is metastable [1] and can be transformed to the hexagonal wurtzite structure following an annealing process [2],[3]. Film deposits of CdSe can be used for the production of economical photovoltaic cells due to offered heterostructure formations [4], spectrum sensitivity, and energy-gap value (1.74 eV) [5]. A variety of CdSe film deposition techniques i.e. chemical vapour deposition [6], evaporation [7], pyrolysis of organo-metallic compounds, sol-gel synthesis, chemical bath deposition [8]-[11], and electrodeposition [12]-[14] have been widely exploited for producing polycrystalline CdSe films over large areas. The electrodeposition technique may be used to obtain II-VI semiconductor polycrystalline films over conductive or insulating substrates [15]. It is an isothermal process mainly controlled by electrical parameters that are easily adjusted to determine film thickness, morphology, stoichiometry and interparticle separation [16].

This work presents the electrodeposition process of CdSe films on nickel substrate and investigates the electrical properties of Au-CdSe-Ni structures for possible photovoltaic conversion.

2 Experimental

2.1 Sample fabrication

Thin films of CdSe were deposited on disc-shaped ($\Phi=15\text{mm}$) nickel bulk substrates consisting of commercial purity nickel (99.9%). The surface of the nickel substrate had been polished to a mirror finish degree by Al_2O_3 paste, cleaned, then etched in 10% HCl solution for 40 s and washed thoroughly in de-ionized water.

The produced CdSe films were electrodeposited potentiostatically in a thermostat-controlled three-electrode cell. The electrodes consisted of a Hg/Hg₂SO₄ reference-electrode, a platinum grid counter-electrode, and a rotating working-electrode formed by the Ni substrate. The electrodes were electrically connected to a CBP bipotentiostat-scan system (Pine Research Instrument).

The deposition bath contained solutions with excess Cd²⁺ (0.2M) from CdSO₄, and small amounts of SeO₂ (1×10^{-3} M). The pH of the deposition bath was adjusted to 2.2 at 25°C, by adding $\approx 10\%$ H₂SO₄. The overall experimental set-up used for the electrodeposition of the CdSe is presented schematically in Fig 1.

In a typical deposition run the bath was first thermostated at the required temperature, which varied from 55°C to 65°C. After the desired bath solution temperature had been attained, the working electrode (i.e. Ni substrate) was suspended in the solution, and it was rotated at 500 rpm. Plating of the working electrode was accomplished at a deposition potential of 1000 mV (vs. the reference electrode of Hg/Hg₂SO₄). Film formation was easy and visible to the naked eye. The deposition process was carried out for 20 min to achieve a uniform glossy-black film of CdSe. For these electrochemical conditions the obtained CdSe film had a uniform thickness of 2 μm , as revealed by crystallographic cross-sections and SEM observations, Fig. 2(a).

Smaller electrodeposition intervals resulted to different film thickness and different surface color. For a 2 min deposition interval the obtained film was estimated to be of the order of 200 nm and the provided color was yellow-gold, Fig. 2(b).

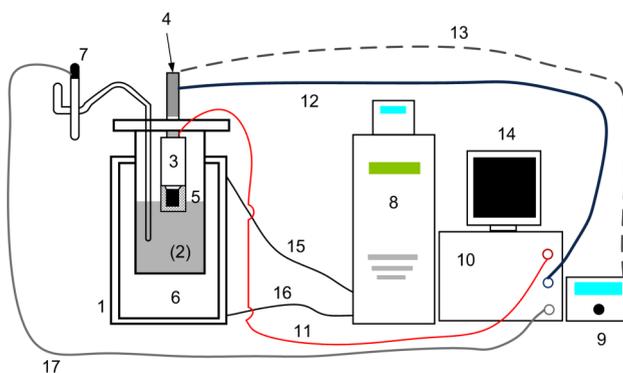


Fig 1. Experimental setup of the electrodeposition system. 1. Cell with double glazing allowing circulation of the heating liquid, 2. Deposition bath, 3. Counter-electrode, 4. Rotating shaft, 5. Working electrode: nickel cylindrical substrate, 6. Electrolytic cell, 7. Reference-electrode, 8. Heating-liquid circulator, 9. Rotating-speed controller, 10. Bipotentiostat-unit, 11. Electrical connection between bipotentiostat and counter electrode, 12. Electrical connection between bipotentiostat and working electrode, 13. Electrical connection between shaft and spin controller, 14. PC platform, 15. Heating liquid inwards, 16. Heating liquid outwards, 17. Electrical connection between bipotentiostat and reference electrode.

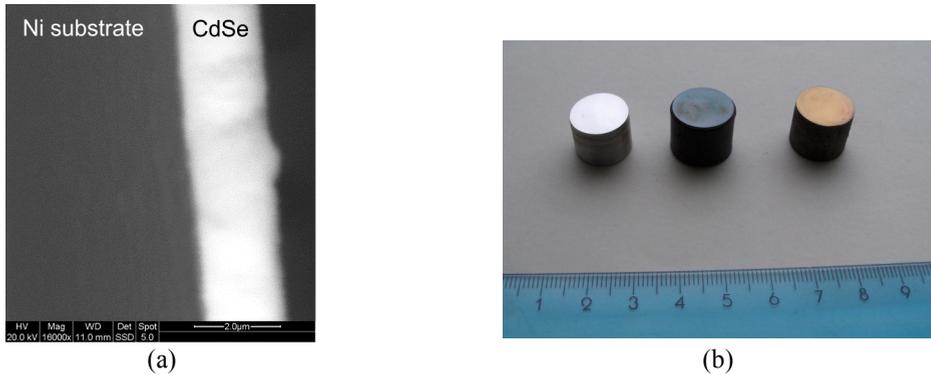


Fig.2. (a) Cross-section of fabricated deposit, as viewed by SEM. The CdSe film is 2 μm thick for a 20 min electrodeposition interval. **(b)** Specimen geometry and surface color obtained under various deposition intervals. From left to right: *i)* blank Ni substrate, *ii)* 2 μm CdSe film obtained after 20 min electrodeposition, *iii)* 200 nm CdSe deposit obtained within electrodeposition intervals of 2 min.

The CdSe deposits on the Ni substrate could be annealed in a high purity dry N₂ gas, thus preventing possible oxidation. The prepared CdSe samples were placed in a closed Ultra High Vacuum (UHV) stainless steel cylindrical reactor having an internal volume of 1 litre, and then the vessel was evacuated towards 10⁻⁴ mbar, to have it filled with N₂ gas. Low residual oxygen concentration in the reactor was confirmed in situ by quadrupole mass analysis. The applied thermal cycle consisted of an 1 h temperature rising profile towards its set point temperature (in the range of 250 to 500°C), where it remained over a period of 5 h, followed by the cooling stage attained by natural heat convection (total thermal treatment duration 24 h). The temperature profile in the reactor was measured via a thermocouple, while the external surface temperature of the vessel was monitored via an infrared thermometer.

2.2. Sample characterization

The produced CdSe films were characterized by X-Ray diffraction (XRD) analysis to identify crystal phases. A Siemens 5000 X-ray diffractometer system with Cu-Kα radiation ($\lambda = 0.154$ nm) was used and the settings were: 20 kV and 5 mA.

The morphology of the surface was studied by a scanning electron microscope (SEM) in a FEI Quanta 200 system.

Gold contacts were placed by evaporation on top of the CdSe surface. Alternatively, electrical point contacts were produced by pressing mechanically an 1 mm diameter gold spherical probe on the CdSe surface. The current-voltage characteristics of the Ni/CdSe/Au structures was investigated by employing a computer controlled pA meter-DC voltage source (Agilent 4140B). The applied voltage varied from -2 V to 2 V, with an increment of 0.01 V. The device under test was placed in a Faraday cage (Agilent 16054A) to exclude the presence of light and electromagnetic noise.

3 Results and Discussion

3.1 XRD Characterization

Representative XRD results for the CdSe films formed under bath deposition temperature 55°C, 60°C and 65°C, are given in Fig. 3. These spectra suggest the formation of compact layers of cubic

zinc-blende CdSe structure, and -depending on the exact formation conditions- they may exhibit a more or less pronounced (111) preferred orientation. This orientation preference is maximised for electrodeposits formed under 65°C. Diffraction peaks for elemental Cd (angle $2\theta = 31.8^\circ$) or c-Se ($2\theta = 30.0^\circ$), m-Se ($2\theta = 24.8^\circ$) h-CdSe ($2\theta = 31.7^\circ$) are not observed. All spectra exhibit reflections originating from the Ni substrate ($2\theta = 44.5^\circ, 51.8^\circ, 76.4^\circ$). All XRD spectra of CdSe samples formed under different bath solution temperature exhibit strong reflections from the (111) plane of the cubic CdSe microcrystal (angle $2\theta = 25.3^\circ$).

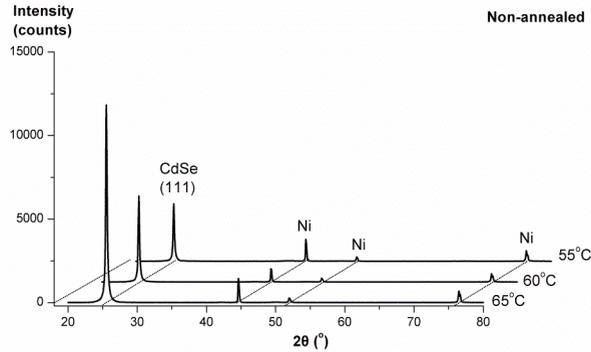


Fig. 3. Typical XRD spectra of the as-produced CdSe electro-deposits on Ni substrates under various bath-formation temperatures reveal cubic zinc-blende structure with (111) orientation.

The preferential growth of the CdSe crystals in (111) is further intensified following thermal treatment in N_2 gas. As shown in Fig 4, for the electrodeposits produced under 65°C, the diffraction peaks of the CdSe zinc-blende cubic structure ($2\theta = 25.3^\circ$) intensify after annealing. Note that, CdSe (111) orientation is enhanced for samples formed under electrodeposition-bath temperature 65°C, compared to any sample prepared under a different solution temperature.

According to various workers in this field, the cubic phase of CdSe is generally obtained when the material is grown from chemical reactions [8],[17],[18]. For these growing conditions, the obtained cubic CdSe (CAS registry number [1306-24-7]) is characterized as metastable, and converts to wurtzite hexagonal structure after annealing at 650°C for 15 min in an inert atmosphere [1],[19],[20]. However, in this work, for the produced electrolytic deposits this crystallographic transformation was not noticed after annealing.

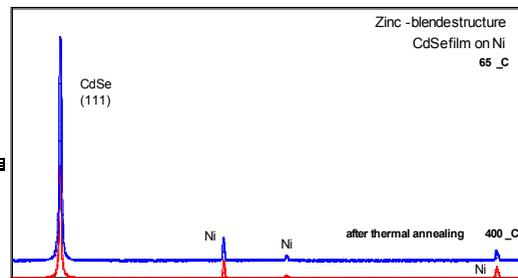


Fig. 4. XRD spectra of CdSe prepared under bath-solution temperature 65°C, prior (*lower spectrum*) and following annealing (*upper spectrum*).

3.2 SEM Characterization

Surface morphology of the CdSe films was investigated by SEM. The highly crystallized CdSe/Ni samples are generally stoichiometric and exhibit optically a mirror-like surface deprived of any irregularities. The obtained micrographs show compact polycrystalline films of regular morphology. Fig. 5 provides representative surface morphology prior thermal annealing of the CdSe films deposited under bath solution temperature 60°C and 65°C. According to these SEM micrographs the appearance of the as-produced deposits is quite regular, often presenting some granular outgrowths. The surface morphology of the CdSe films formed at 60°C exhibits spherical grains (up to 2 µm in diameter) that are uniformly distributed over the surface. As bath temperature increases towards 65°C, the grain size is increased (hillocks up to 4 µm in diameter).

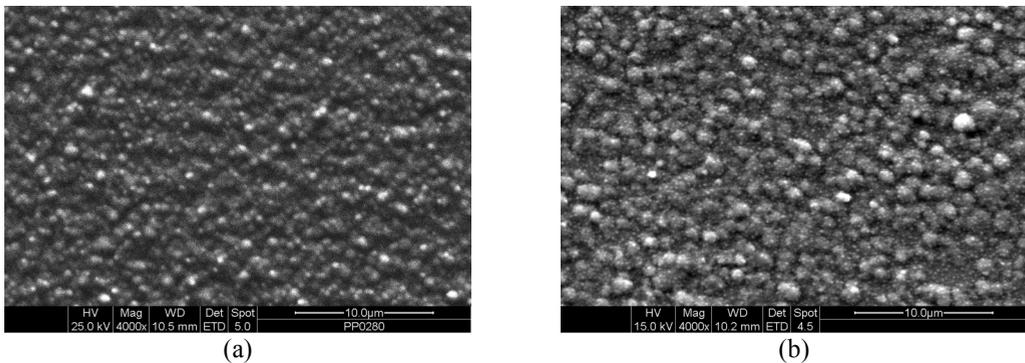


Fig. 5. SEM micrographs of 2µm thick CdSe films on Ni substrate fabricated under different conditions: (a) electrodeposition bath at 60°C and (b) electrodeposition bath at 65°C.

Fig. 6 provides the induced changes by the thermal annealing on the CdSe surface. Here, the size of the surface hillocks appears increased, but with significantly reduced concentrations. The uniformity of the crystals produced under 65°C is significantly enhanced. All deposits lack of pinholes or cracks and are well adhered to their Ni-substrates. For the surfaces presented in Fig. 6 the thermal treatment was performed over a period of 5 h, in dry N₂ gas, at 500°C.

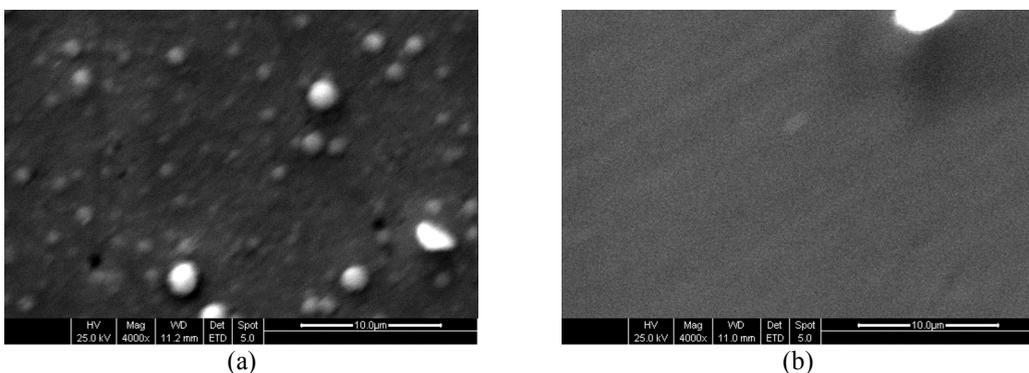


Fig. 6. SEM micrograph of 2µm thick CdSe films on Ni substrate, following annealing at 500°C. (a) electrodeposition bath at 60°C and (b) electrodeposition bath at 65°C.

3.3 Electrical Characterization

Semi-log I-V plots obtained across the Ni-CdSe-Au structure are presented in Fig. 7. Here, the current-voltage plots provide forward and reverse polarity current values in the same quadrant, for comparison purposes. Each plot presents the current voltage characteristics of the film prior and following thermal treatment.

According to the obtained results the produced CdSe deposits under low bath solution temperature (55°C) do not exhibit any rectification properties. Lack of rectification properties may be attributed to induced changes in the semiconductor electron affinity [21] for the deposited CdSe structures under different bath solution temperatures. It may also be related to localized narrow impurity bands formations within the band gap of the semiconductor stimulated by the presence of impurities [22] or lattice disorders near the surface. Some degree of current rectification is observed for the as-produced deposits under 65°C. The observed differences in the electrical response of the examined Ni-CdSe structures formed under different bath temperatures are in good agreement with SEM characterization, where the surface morphology of the CdSe deposits alters significantly with bath solution temperature values.

After annealing in N₂ gas, the conductivity of CdSe is significantly enhanced. This intensifies the current flowing through the Ni-CdSe-Au structure by several orders of magnitude (10³-10⁴ times). This large current increase may only be attributed to a carrier concentration change in the semiconductor, as the device area remains unaltered and any carrier mobility modifications (due to a change in the effective mass) cannot account for the excessive conductivity increase. The rectification properties become more intense and this could be related to crystal quality enhancement (as also implied by the XRD results). Rectifying response of the Ni/CdSe/Au structure is essential in utilizing the material for photovoltaic conversion, since the built-in potential barrier is exploited to separate the produced electron-hole pairs [23].

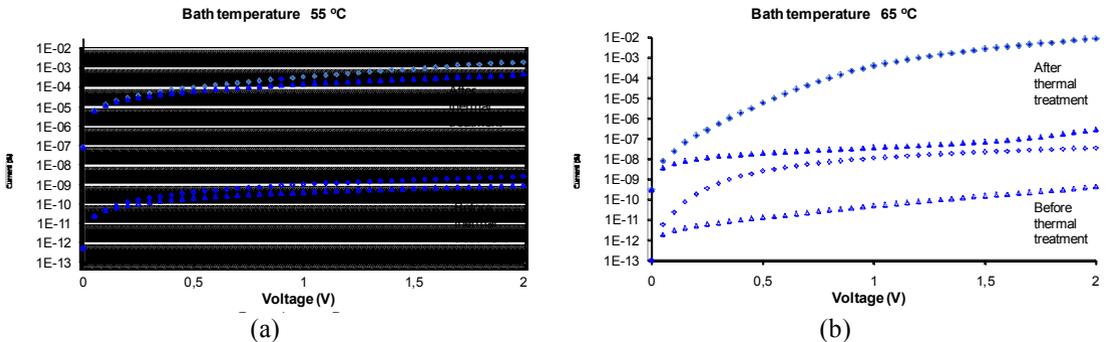


Fig. 7. The current-voltage characteristics (in the dark) for the CdSe films on Ni substrates may vary significantly according to the bath solution temperature during electrodeposition: (a) electrodeposition bath at 60°C and (b) electrodeposition bath at 65°C.

As far as the photovoltaic conversion is concerned, the illumination of the Au-CdSe-Ni structure (from the Au electrode) has no effect provided the CdSe film thickness is of the order of a micron. However, as the CdSe film thickness becomes comparable to the diffusion length for holes and electrons in CdSe (i.e. 200 nm) the generated photocurrent drastically affects the overall current-voltage characteristics, as shown in Fig. 8. Here, the I-V response of a non-annealed Ni - 200 nm CdSe film - Au structure is investigated both: (a) in the dark, and (b) under diffused radiation excitation (having irradiance ≈ 0.5 mW/cm²). Here, the photons impinging from the side of the Au electrode which is formed by a mechanically sustained point-contact can generate a photocurrent. As

indicated by the I-V in Fig 8b, the structure can generate power which for the specific illumination conditions are characterized by $I_{SC} = 8.10^{-12}$ A, and $V_{OC} = 0.04$ V.

Though conventional photovoltaic cells generate their power in the 4th quadrant, as shown in Fig 9a, this structure behaves entirely differently as it can generate power in the 2nd quadrant, as shown in Fig 9b. This practically means that the produced photocurrent is not algebraically subtracted from the (negative) reverse bias current as is the case for p-n diodes, but it is added algebraically the (negative) reverse bias current flowing through the device. This response may give rise to a new family of devices for photovoltaic conversion. To understand their operating principle a detailed investigation based upon Schottky barrier formations and metal Fermi-level pinning on either side of the CdSe semiconductor will have to be considered.

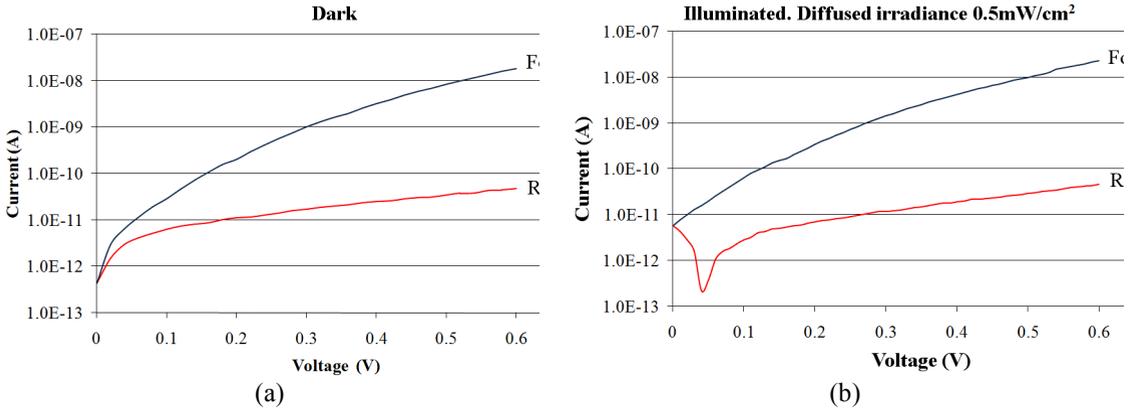


Fig. 8. The current-voltage characteristics (a) in the dark and (b) under illumination for a 200nm CdSe film incorporated in the Ni-CdSe-Au structure provides photovoltaic conversion in the 2nd quadrant.

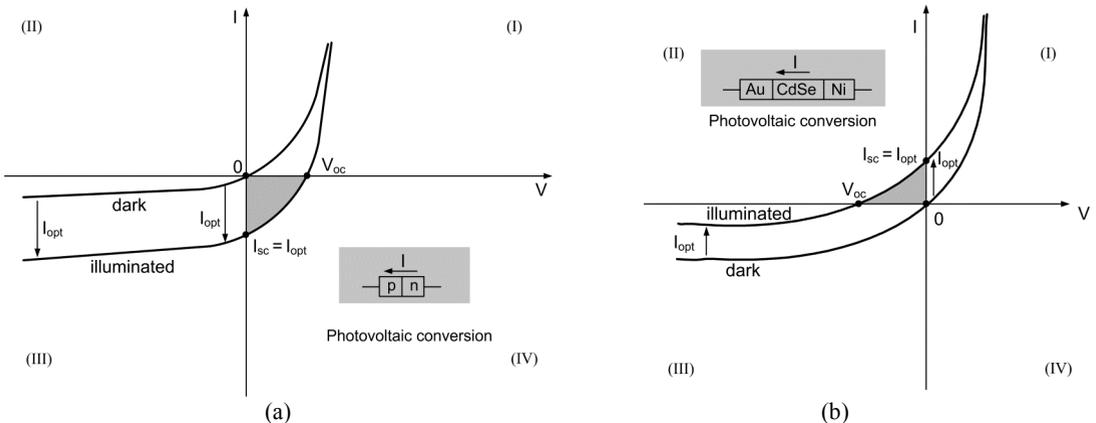


Fig. 9. The current-voltage characteristics for: (a) conventional photovoltaic cell producing power in 4th quadrant, and (b) the Ni-CdSe-Au structure producing power in 2nd quadrant.

4 Conclusions

Electrolytical deposition of CdSe on Ni substrates has been investigated. The fabricated samples were characterized prior and following thermal annealing at 500°C in pure nitrogen gas. The results show that:

- According to the XRD spectra the obtained CdSe films exhibit the cubic zinc-blende structure even after annealing.
- The bath solution temperature affects the overall electrical properties and surface morphology of the CdSe films.
- SEM micrographs show compact polycrystalline films of regular morphology. Microscopic appearance is quite regular, presenting spherical hillocks/grains. Under thermal treatment the concentration of the grains may vary and it tends to form a homogeneous crystal.
- The measured I-V characteristics exhibit rectification that can be utilized for photovoltaic conversion. The Ni-CdSe-Au structure may exhibit rectifying properties depending on the bath deposition temperature (60°C - 65°C).
- Rectification does not occur when the electrodeposits are formed under lower temperature baths (55°C), in which case ohmic characteristics are encountered across the metal-semiconductor-metal structures.
- Photovoltaic conversion is possible when the film thickness becomes comparable to the diffusion length for holes and electrons in CdSe (i.e. 200 nm).
- Such structures can generate power in a different way compared to the conventional photovoltaic cells.

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