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ZnSe-BASED SOLAR-BLIND ULTRAVIOLET PHOTODETECTORS WITH DIFFERENT SCHOTTKY CONTACT METALS

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We report on the selection of contact metallisations for ZnSe-based metal-semiconductor-metal ultraviolet photodetectors. Our evaluation is based on Ni/Au, Cr/Au, and hybrid Ag-nanowire contacts. Low values of dark current of 0.32 nA, 0.82 nA and 1.64 nA at bias voltage of 15 V were achieved for photodetectors with Ag-NW, Ni/Au and Cr/Au interdigital contacts, respectively. The best performance of our ZnSe-based ultraviolet photodetectors is observed for Ni/Au interdigital contacts. This is due to the higher Schottky barrier height, which is equal to ~ 1.49 eV for Ni/Au contacts in comparison with ~ 1.26 eV for Cr/Au contacts. A very high responsivity of 5.40 AW^{-1} at bias voltage of 15 V for light with a wavelength of 325 nm is obtained for devices with Ni/Au interdigital contacts. Moreover, the maximum of photocurrent on/off ratio of 20342 and minimum of NEP of ~ 3×10^{-15} W $Hz^{-1/2}$ at bias voltage of 15 V was achieved for this type of device.

Keywords*: zinc selenide, metal-semiconductor-metal structures, Schottky diodes, ultraviolet photodetectors, impact ionization.*

FOTODETECTOARE ULTRAVIOLETE SOLAR-BLIND PE BAZA ZnSe CU DIFERITE METALE DE CONTACT SCHOTTKY

Se raportează despre alegerea metalelor de contact pentru fotodetectoarele ultraviolete de tip metal-semiconductor-metal bazate pe ZnSe. Evaluarea noastră se bazează pe contactele Ni/Au, Cr/Au și pe hibridul Ag-nanofir. Valorile scăzute ale curentului întunecat de 0,32 nA, 0,82 nA și 1,64 nA la tensiunea de polarizare de 15 V au fost atinse pentru fotodetectoarele cu contacte interdigitale Ag-NW, Ni/Au și, respectiv, Cr/Au. Cea mai bună performanță a fotodetectoarelor ultraviolete bazate pe ZnSe se observă pentru contactele interdigitale Ni/Au. Acest lucru s-a dovedit a fi posibil datorită înălțimii mai mari a barierei Schottky care este egală cu ~ 1,49 eV pentru contactele Ni/Au, în comparație cu ~ 1,26 eV pentru contactele Cr/Au. O sensibilitate foarte mare de 5,40 A W^{-1} la tensiunea de polarizare de 15 V pentru lumină cu lungimea de undă de 325 nm este obținută pentru dispozitivele cu contacte interdigitale Ni/Au. Raportul maxim de pornire/oprire a fotocurentului egal cu 20342 și minimul puterii echivalente de zgomot (NEP) egale cu ~ 3×10^{-15} W $Hz^{-1/2}$ la tensiunea de polarizare de 15 V au fost atinse pentru acest tip de dispozitiv.

Cuvinte-cheie*: seleniură de zinc, structuri metal-semiconductor-metal, diode Schottky, fotodetectoare ultraviolete, ionizare prin coliziuni.*

Introduction

Wide-bandgap semiconductors such as ZnSe are attractive semiconductors for fabrication of ultraviolet (UV) photodetectors due to their large bandgap energy (2.67 eV at 300 K), high electric field strength of breakdown (~ 1 MV/cm), as well as high resistance to intense UV and X-ray radiation [1-5]. Most commercial UV-photodetectors are based on Si or GaAs semiconductors, which require a filter to eliminate visible and infrared light. Moreover, the intense UV radiation induces aging effects in Si-based photodetectors that leads to its degradation. To solve this issue, the bulk high-resistivity ZnSe could be used for fabrication of stable high-performance UV photodetectors with metal-semiconductor-metal structure, as we have shown recently [6]. The UV detectors are usually based on the following structure types: planar Schottky diode, vertical Schottky diode, p-i-n photodiode or metal-semiconductor-metal (MSM) photodiode. The last MSM structure is of special interest since it could be used for monolithic integration with field effect transistors. MSM UV photodetectors are unipolar devices with two back-to-back Schottky metal/semiconductor junctions formed on the same semi-insulating semiconductor surface. Vigue et al. [2] experimentally investigated ZnSe-based UV photodetectors with different structures and found that at room temperature the maximum responsivities are of 0.17 A/W at -2 V for a p-i-n-photodiode based on ZnBeSe/ZnMgBeSe, and of 0.13 A/W at 20 V for Schottky diodes (vertical and planar) and MSM photodetectors. A similar value of responsivity of 0.13 A/W at 1 V has been reported by Lin et al. [7] for ZnSe-based MSM photodetectors with transparent Indium Tin

Oxide (ITO) contact electrodes. The UV photodetectors based on MSM structures feature a very low capacitance in the fF-range, and thus could operate at high frequencies. Moreover, due to its structure, MSM photodetectors have a high resistivity, and a high bias voltage can be applied. This opens up the possibility to enhance the responsivity of ZnSe-based MSM UV photodetectors using internal gain mechanisms employing impact ionisation (avalanche breakdown effect) due to the higher internal electric field strength. ZnSe-based UV-photodetectors reported up to now are based on an epitaxial ZnSe active layer grown on a GaAs substrate by molecular beam epitaxy (MBE) or metal-organic chemical vapor deposition (MOCVD) techniques. At intense UV radiation, this thin epitaxial ZnSe layer could be damaged. In this case, a polycrystalline and block-structured ZnSe is a more suitable material for the fabrication of UV MSM photodetectors for intense UV radiation.

To achieve enhanced performance characteristics of UV photodetectors, a large Schottky barrier height is necessary at the metal-semiconductor interface. A large barrier height would lead to a small leakage current and high breakdown voltage. This results in improving the responsivity and rejection rate of such UV photodetectors. Among different metals, the metals with high work functions like Ni, Cr, Ag or Au are required to achieve a large Schottky barrier height on ZnSe [8-12]. In this work, we report on fabrication and study of the effect of different metal contacts (hybrid Ag-nanowire (Ag-NW), Cr/Au and Ni/Au) on performance of ZnSe-based MSM UV photodetectors. We show that the best one is the device with Ni/Au interdigital contacts, due to the higher Schottky barrier height of Ni-ZnSe interface.

Experimental

High resistivity (~ 10^{12} Ω cm) bulk ZnSe crystals grown by the vapour phase method were used as an active layer of UV photodetectors. The as-grown undoped ZnSe crystals were cut into pieces with dimensions of 5 mm × 10 mm × 1 mm, and polished mechanically and chemically in a 7% solution of Br-CH_3OH. After that, they were boiled in 40% NaOH and cleaned in acetone and in oxygen plasma. The Schottky contacts were fabricated by e-beam evaporation of 25 nm Cr or Ni followed by a thermally evaporating of 140 nm Au, and performing standard photolithographic and lift-off processes. A 500 nm dielectric Si_xN_y passivation layer was placed above the metallic structure in order to prevent electric breakdown [2]. Two types of ZnSe-based MSM UV photodetectors were fabricated as shown in Fig.1: with interdigital contacts (Fig.1(a)) and with conventional contacts (Fig.1(b)). For both typed of photodetectors, the active area is 10 μm x 10.5 μm with 3 μm × 10.5 μm contact pads. The UV photodetector with interdigital contacts consists of 6 pairs of 0.5 μm width metallic finger contacts with the distance of 1.5 μm between fingers as shown in Fig.1(a).

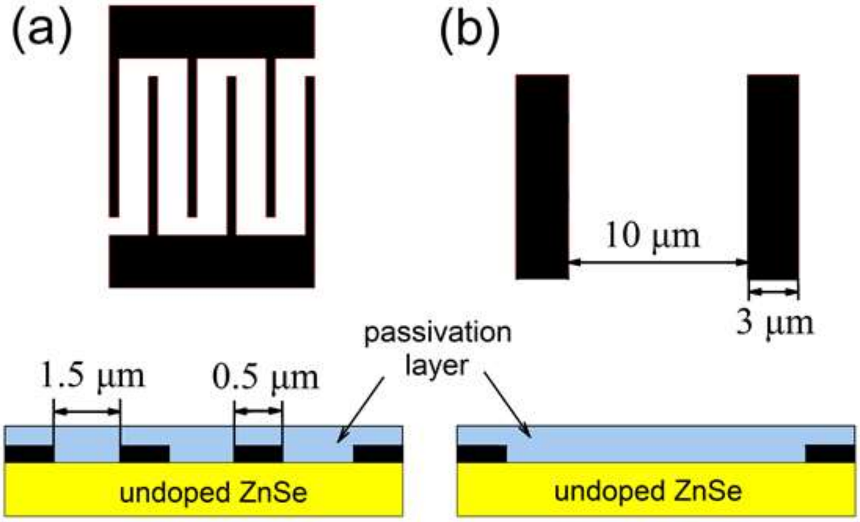

Fig.1. Schematic structure of ZnSe-based metal-semiconductor-metal UV photodetectors: (a) photodetector with interdigital contact; (b) photodetector with conventional contacts. The contact pads without passivation layer are outside the active region (is not shown here).

Also, a photodetector with hybrid contacts has been fabricated: one of contacts is conventional Ni/Au contact and the second one is Ag-nanowire (Ag-NW) contact. A simple spin coating method was used to distribute a commercially available Ag-NWs over the ZnSe substrate. The diameter varied only slightly for the commercial nanowires. The nanowires were randomly distributed and have different positions. The alignment of the Ag-NWs has been performed using the dielectrophoresis method. The investigated photodetector had a nanowire diameter of 120 nm and a tip-tip gap of 1 μm.

The current-voltage characteristics of fabricated UV photodetectors in the dark and under UV illumination were measured using a Keithley 2612 multimeter. The applied bias voltage was varied from 0 V to 15 V. The photocurrent was excited by a 325-nm Cd-He laser with output optical power of 56.5 mW and beam spot diameter of 1.56 mm. The illumination laser power on the active area of the photodetectors was estimated to be equal to 3.1 μW. For the measurements of time-dependent characteristics of the photocurrent, the UV laser light was modulated by a chopper with a frequency range of 20 Hz – 1 kHz, a load resistance of 9.9 MΩ was connected in series with the fabricated ZnSe-based MSM UV photodetector and DC voltage source of 20 V, and the relaxation curves of voltage from load resistance were measured by Tektronix TDS 210 oscilloscope.

The performance of the UV photodetectors was characterised by its responsivity R, the detectivity D^*, and noise equivalent power (NEP) which are defined as follows:

$$R = \frac{I_{photo} - I_{dark}}{P_{ill}}, \qquad D^* = \frac{R\sqrt{A}}{\sqrt{2eI_{dark}}}, \qquad NEP = \frac{\sqrt{2eI_{dark}}}{R} \qquad (1)$$

where I_{photo} is the photocurrent of the photodetector under UV illumination, I_{dark} is the dark current, P_{ill} is the illumination power on the photodetector, A is the active area of the photodetector, and e is elementary charge. Here, the estimation of the detectivity D^* by formula (1) is based on the assumption that shot noise is the primary source of noise in the detector.

Results and discussion

The current-voltage (I-V) characteristics of the ZnSe-based MSM UV photodetectors with Ni/Au interdigital and conventional contacts in the dark and under illumination of UV light are shown in Figs.2(a) and 2(b), respectively. It can be seen that, for both types of UV photodetectors, the dark current-voltage dependences show a behaviour, which is typical for a Schottky diode. The similar behaviour of I-V characteristics is characteristic for ZnSe-based UV photodetectors with Cr/Au contacts as we showed early [6].

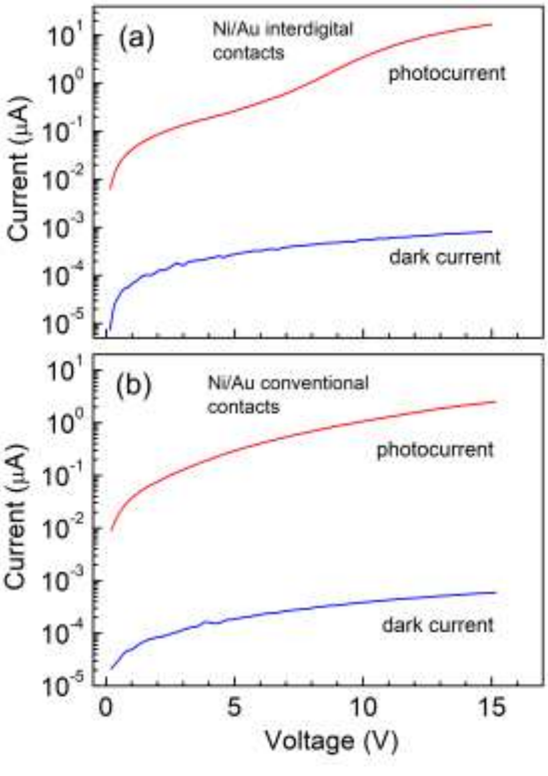

Fig.2. Current-voltage characteristics of ZnSe-based MSM UV photodetectors with Ni/Au interdigital contacts (a) and Ni/Au conventional contacts (b).

The current-voltage (I-V) characteristics of the two ZnSe-based MSM UV photodetectors (with interdigital and conventional Ni/Au contacts) in the dark and under illumination of UV laser light are shown in Figs.2(a) and 2(b). It can be seen that, for both samples, the dark current practically linearly increases with increasing bias voltage. When the bias voltage of 15 V is applied, the maximum dark current is equal to 0.59 nA and 0.82 nA for photodetectors with conventional and interdigital contacts, respectively. Under UV laser illumination, the behaviour of I-V characteristics shows significant changes and becomes non-linear: at first, the photocurrent increases almost linearly with applied voltage for $U < 8$ V, and significantly increases when the applied voltage is > 10 V that is caused by the avalanche effect. From the I-V dependences, maximum values of dark current have been estimated to be 1.64 nA and 0.82 nA at bias voltage of 15 V for the devices with Cr/Au and Ni/Au interdigital contacts, respectively.

To investigate the mechanisms of current transport in the UV photodetectors in the dark and under illumination, the *I-V* curves for both photodetectors were plotted also in semi-logarithmic scale (Figs.2(a) and 2(b)). For both devices, the dark *lg(I)-V* curves have two linear parts with different slopes. The linear dependence of dark current at voltages lower than 2 V indicate a thermionic mechanism of electronic transport via the Schottky barrier formed by metal (Au/Cr or Au/Ni)/semiconductor (ZnSe). Due to their amphoteric properties [10], Au atoms may create both donor and acceptor centres during diffusion to ZnSe, while Cr and Ni create deep acceptor centres in ZnSe[11], which compensate for uncontrolled background donor impurities in ZnSe. Therefore, Cr/Au and Ni/Au contacts are attractive for the fabrication of the Schottky barrier structures with good characteristics. The Schottky barrier height formed by Au/Cr or Ni/ZnSe interdigital contacts in fabricated photodetectors was estimated to be ~ 1.26 eV and ~ 1.49 eV, respectively, using the empirical formula [12]: $\varphi_B = 0.42\varphi_M - 0.63$ [eV], where φ_B is the Schottky barrier height, φ_M is the work function of metal (in our case is the work function of Cr or Ni). These values are close to the half bandgap energy of ZnSe, which is the optimal condition for obtaining the lowest dark current and better performance of Schottky diodes [15].

The photocurrent on/off ratio of the UV photodetectors, defined as ratio of photocurrent to the dark current, is also increased with increasing the bias voltage for both types of UV photodetectors as shown in Fig.3. This ratio achieves a maximum value at a bias voltage of 15 V, which is equal to 4219 and 20342 for the devices with Cr/Au and Ni/Au interdigital contacts, respectively. These peak values of photocurrent on/off ratio are more than 1-2 orders of magnitude higher than that reported earlier for UV-photodetectors based on bulk ZnSe, ZnSe- or ZnSe/ZnO-based nanostructures [1,2,13,14].

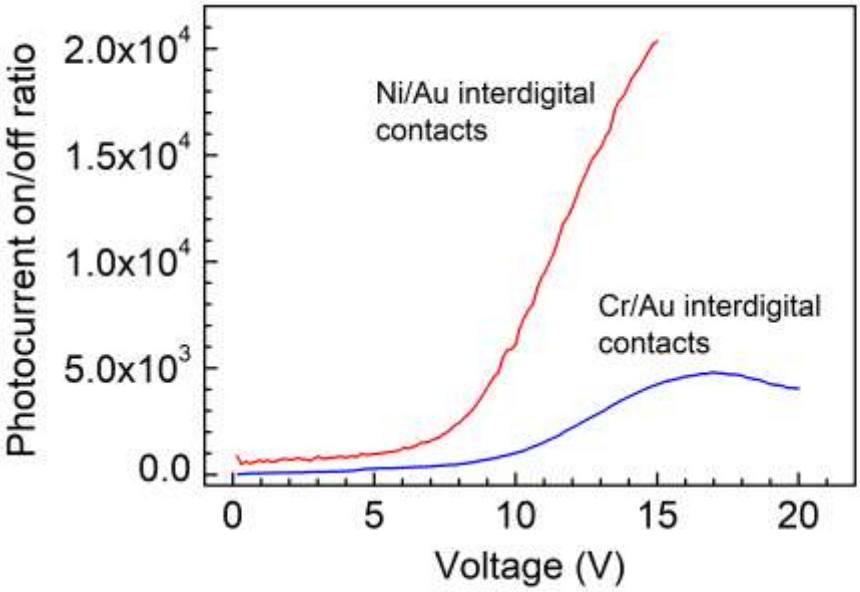

Fig.3. Dependence of photocurrent on/off ratio of ZnSe-based MSM UV photodetectors with Cr/Au and Ni/Au interdigital contacts as function of applied bias voltage.

The responsivity of all fabricated UV photodetectors, measured under applied voltage from 0 to 20 V, is presented in Fig.4(a). The behaviour of responsivity dependences has a similar character to the dependences of photocurrent on/off ratio of the respective UV photodetectors (Fig.3). Maximum values of responsivity of 2.23 A W^{-1} and 5.40 A W^{-1} at bias voltage of 15 V for light with a wavelength of 325 nm is found for the photodetectors with Cr/Au and Ni/Au interdigital contacts, respectively. These values are significantly higher than the maximum value of 0.13 A/W at 450 nm reported by Vigue et al. [2] for different types of ZnSe-based photodetectors. The ideal responsivity for ZnSe-based photodetectors at 325 nm, assuming gain of 1 and external quantum efficiency (EQE) of 100% calculated by formula $R_{\text{ideal}} = q\lambda/(hc)$ gives a value of 0.26 A/W. Taking into account the experimentally-obtained external quantum efficiency (EQE) for a ZnSe MSM photodetector at 450 nm of 35 % [2], we have estimated the maximum internal gain of photocurrent and responsivity to be equal to ~ 50 and ~ 100 for a ZnSe-based MSM UV photodetectors with Cr/Au and Ni/Au interdigital contacts, respectively. The internal gain effect is attributed to the impact ionization in ZnSe due to the high electric field strength, which is equal to about 100 kV/cm at applied bias voltage of 15 V for photodetectors with interdigital contacts.

The noise equivalent power (NEP) dependences of the UV photodetectors, defined as the signal power that gives a signal-to-noise ratio of one in a one hertz output bandwidth and calculated from I-V characteristics, are shown in Fig.4(b). The minimum of NEP of ~ 1 × 10^{-14} W Hz$^{-1/2}$ W^{-1} and ~ 3 × 10^{-15} W Hz$^{-1/2}$ at bias voltage of 15 V was obtained for ZnSe-based MSM UV photodetectors with Cr/Au and Ni/Au interdigital contacts, respectively. These values are comparable or even lower than that for ZnSe-based MSM UV photodetectors reported earlier [2,13].

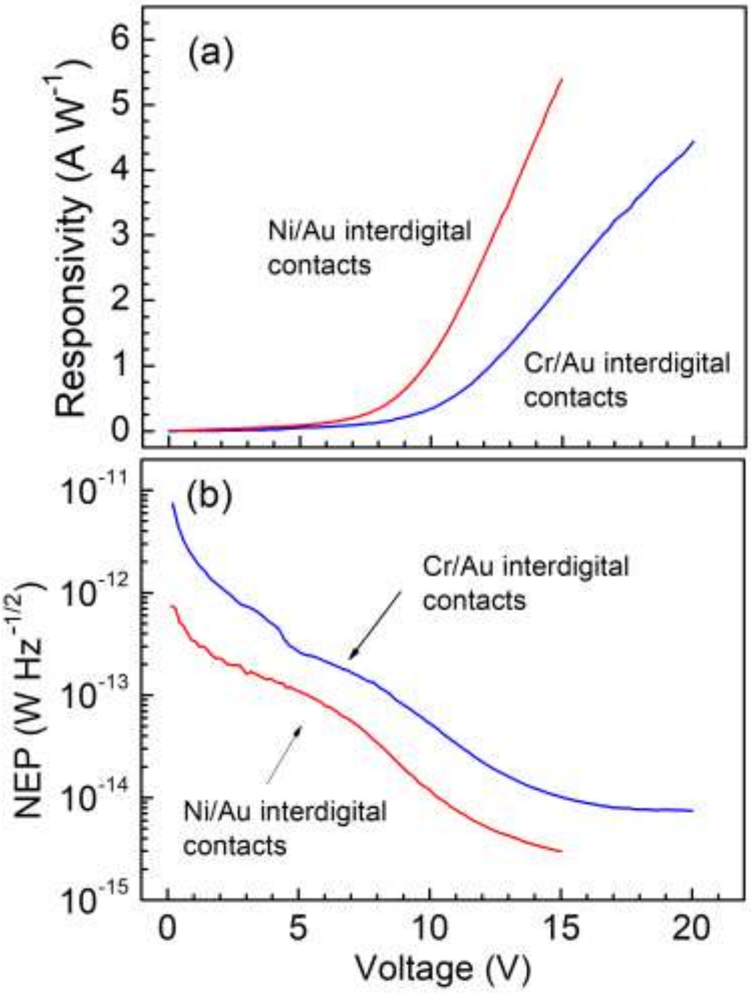

Fig.4. Responsivity (a) and NEP (b) of ZnSe-based MSM UV photodetectors with Cr/Au and Ni/Au interdigital contacts.

The current-voltage (I-V) characteristics of the ZnSe-based MSM UV photodetectors with hybrid Ag-NW contacts in the dark and under illumination of UV laser light are shown in Fig. 5. It can be seen that, for both samples, the dark current practically linearly increases with increasing bias voltage. When the bias voltage of 15 V is applied, the maximum dark current is equal to 0.36 nA. Under UV laser illumination, the behavior of I-V characteristics shows significant changes and becomes non-linear.

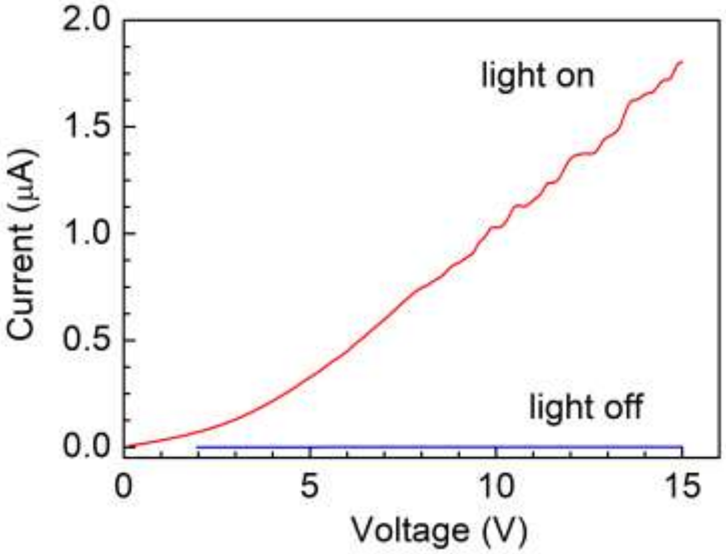

Fig.5. Current-voltage characteristics of ZnSe-based MSM UV photodetectors with hybrid Ag-NW and Ni/Au contacts.

The responsivity of ZnSe-based photodetector with hybrid Ag-NW contact, measured under applied voltage from 0 to 15 V, is presented in Fig.6. The behaviour of responsivity dependence has a similar character to the photocurrent dependence of the respective UV photodetector (Fig.5). Maximum value of responsivity of 0.58 A W^{-1} at bias voltage of 15 V for light with a wavelength of 325 nm is found for this device. This value is few times higher than the maximum value of 0.13 A/W at 450 nm reported by Vigue et al. [2] for different types of ZnSe-based photodetectors, but lower than the responsivity of devices with Cr/Au and Ni/Au inter-digital contacts.

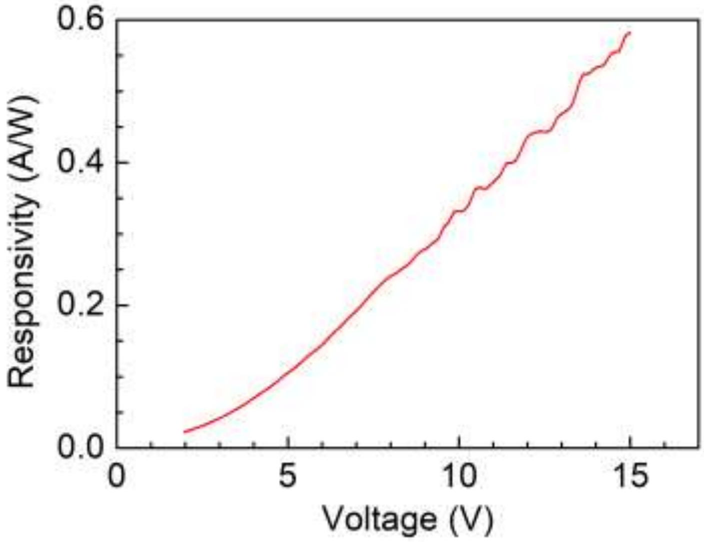

Fig.6. Responsivity of ZnSe-based MSM UV photodetectors with hybrid Ag-NW – Ni/Au contacts.

The detectivity characteristics of the photodetector with Ag-NW contacts, calculated from I-V characteristics, are shown in Fig.7. This dependence of detectivity vs. applied bias voltage has a V-shape behaviour and, at bias voltage above 3V, practically repeats the behaviour of responsivity curves shown in Fig.6. A maximum value of detectivity of ~ 5.49×10^{10} cm $Hz^{1/2}$ W^{-1} at 15 V was obtained for this device. This value is comparable with detectivity values for ZnSe-based UV photodetectors with Cr/au and Ni/Au contacts (Table).

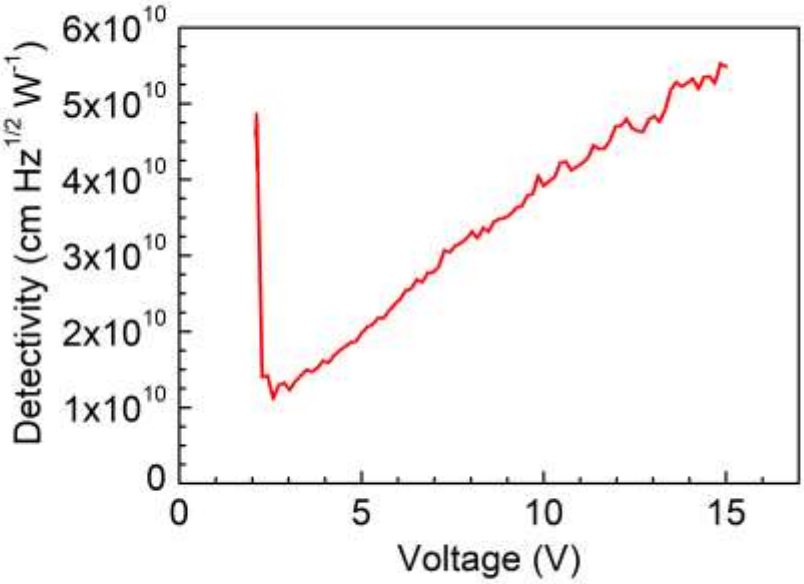

Fig.7. Detectivity of ZnSe-based MSM UV photodetectors with hybrid Ag-NW – Ni/Au contacts.

The measurements of time-dependent photocurrent were carried out using a load resistance of 9.9 MΩ connected in series with ZnSe-based MSM UV photodetectors. The response times estimated from the relaxation characteristics were in the range of 0.15-0.25 ms for photodetectors with conventional contacts, and were in the range of 0.10-0.16 ms for photodetectors with interdigital contacts, respectively. These values of response time are about 2-4 orders of magnitude lower than the reported response times for photodetectors based on bulk and nano-ZnSe or ZnO/ZnSe nanowires [1,2,7,13,14]. Moreover, as reported by Monroy et al. [16], the response time is linearly dependent on load resistance and can be reduced by 2-3 orders of magnitude by reducing the load resistance to kΩ-range. The maximum bandwidth of ZnSe-based MSM UV photodetectors could be limited either by the *RC* time or by the carrier transit time. Taking into account the mean mobility value of 300 cm^2/Vs for undoped ZnSe at 300 K [10] and capacitance of the fabricated photodetectors of ~ 3 fF, we have estimated the values of transit time of 8 ps and 320 ps, and the *RC* time of 17 μs and 56 μs for the photodetectors with and without interdigital contacts, respectively. These results indicate that the *RC* time of the measurement system is the main limiting factor of frequency bandwidth of ZnSe-based MSM UV photodetectors.

The characteristics of all fabricated ZnSe-based UV photodetectors with different contacts are summarized in Table. As can be seen from the Table, among all fabricated ZnSe-based photodetectors, the better one is the device with Ni/Au interdigital contacts due to the high Schottky barrier height of Ni-ZnSe. Meanwhile, the device with hybrid Ag-NW contacts has the lowest value of dark current (0.36 nA) and has the lowest capacitance due to the small footprint of the nanowire contact. This device with Ag-NW contact could be attractive for high-speed UV telecommunications and UV-Tomography applications.

Table

Summary of characteristics of ZnSe-based MSM UV photodetectors with different contacts

Sample No.	**Contacts type**	**Bias voltage 15 V @ 325 nm**			
		Dark current (nA)	**Photocurrent on/off ratio**	**Responsivity (A W^{-1})**	**Detectivity 10^{10} (cm Hz$^{1/2}$ W^{-1})**
#1	Ni/Au interdigital	0.82	20342	5.40	33.7
#2	Ni/Au conventional	0.59	4140	0.79	5.80
#3	Cr/Au interdigital	1.64	4219	2.23	9.86
#4	Cr/Au conventional	0.71	5418	1.25	8.35
#5	Ag-NW – Ni/Au hybrid	0.36	5006	0.58	5.49

Conclusion

ZnSe-based metal-semiconductor-metal ultraviolet photodetectors with Ag-NW, Cr/Au and Ni/Au contacts have been fabricated and investigated. Low values of dark current of 0.32 nA, 0.82 nA and 1.64 nA at bias voltage of 15 V were achieved for photodetectors with Ag-NW, Ni/Au and Cr/Au interdigital contacts, respectively. The lower values of dark current for UV photodetectors with Ni/Au interdigital contacts is due to the higher Schottky barrier height, which is equal to ~ 1.49 eV for Ni/Au contacts in comparison with ~ 1.26 eV for Cr/Au contacts. Maximum responsivity of 2.23 A W^{-1} and 5.40 A W^{-1} at bias voltage of 15 V for light with a wavelength of 325 nm is obtained for ZnSe-based MSM UV photodetectors with Cr/Au and Ni/Au interdigital contacts, which indicates high internal gain of ~ 50 and ~ 100, respectively. Moreover, the minimum value of NEP of $\sim 3 \times 10^{-15}$ W $Hz^{-1/2}$ at bias voltage of 15 V was achieved for the device with Ni/Au interdigital contacts at room temperature, that is ~ 3.3 times lower than that for the devices with Cr/Au interdigital contacts. The device with hybrid Ag-NW contact at bias voltage of 15 V has a maximum photocurrent on/off ratio of 5006 and a maximum responsivity of 0.58 A W^{-1}, respectively. The measured response times of all fabricated UV photodetectors is in the μs-range and is limited by the *RC* time of the measurement system.

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