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Miniature diode spectrometer design

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ABSTRACT

Standard spectrometers involve prisms or diffraction grating to expand light spectra in space and then each spectral region is measured with a photodetector. The limit for miniaturization of such spectrometers is determined by space allocation for spectra expansion. This limit can be overcome with a proposed spectrometer design which employs the dependence of light penetration depth in semiconductor on spectral wavelength and consumes no need for optical components (prisms or diffraction grating). The principle is realized by silicon semiconductor structure with oppositely directed Schottky barrier and n-p junction, where n-region is the base. By applying external voltage U (- 1V ... + 1V) on this structure, the minimum of the potential is formed in some depth $x = x(U)$ of the semiconductor. The observed photocurrent $I = I(U)$ depends on the integral radiation flux that penetrated the material deeper than x . Absorption coefficient $\alpha(\lambda)$ decreases as λ increases. Therefore by scanning the depth x , the contribution of different radiation components (with different λ) on the final signal is scanned. When Current-Voltage dependence $I(U)$ is observed, a special algorithm can be used to extract the initial radiation spectra from these data. Proposed photodetector-spectrometer has the observation spectral range of 400 - 1100 nm. Reconstructed spectra show the accuracy for the spectral peak determination of 20 - 100 nm. Directions for improvements of the design and calculation algorithm is presented.

Keywords: Spectrometer, Schottky barrier, photodetector, photodiode

1. INTRODUCTION

Spectrometers are used to measure the light spectra. From spectra one can determine characteristics of the source or media where the radiation went through. There are many applications of spectrometers, for example, in environment monitoring - for air and water quality monitoring, remote sensing and volcanic research¹. There was about 7.5 billion \$ market of global spectroscopy in 2014 and estimated to be 9.55 billion \$ market in 2019². Typical spectrometers use prisms or diffraction grating to expand light spectra in space and then use the array of photodiodes or CCD matrices to measure corresponding intensities³. The largest limiting factors for using them in daily applications are their size (no less than few centimeters) and their price (miniature spectrometers with 1 nm resolution costs above 1500 EUR).

Spectroscopy market is very competitive and there are a lot of spectrometer manufacturers in Europe, United States and Japan. At the same time, production of such key spectrometer components as light detectors is mostly controlled by Japanese companies Hamamatsu, Sony and Toshiba. For a European company to enter the spectrometer detector manufacturing business it would require significant investments. At this point, Japanese companies own almost all the know-how and patents to produce low cost detectors with superb technical specifications. The only way to enter the market is with a disruptive technology.

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A new technology was developed theoretically in National Polytechnic University of Armenia where a single diode is used as a spectrometer, and incident light spectra is reconstructed from Current-Voltage characteristic of the diode⁴⁻⁸. Such diode spectrometer is expected to have 200 – 1200 nm measuring range and 1 nm resolution, the same as currently available USB spectrometers. Main advantages of a diode spectrometer compared to an array based detectors are: smaller size achieved by removing the optical path and diffraction gratings, more robust alignment possible as no optical components are present, better sensitivity as no filters, optical paths or diffraction gratings are used, reduced price as no optical components are required. Therefore the proposed diode spectrometer is a good candidate to substitute currently available miniature spectrometers. Due to its miniature size it can be a candidate for first integrated spectrometer for mobile phones.

The design and actual manufacture of proposed diode spectrometer was made by RD Alfa microelectronics. Several iteration of design and tests were made. Results of the third design are described below.

2. THEORETICAL MODEL

The principle of a novel diode spectrometer is realized by silicon semiconductor structure with oppositely directed Schottky barrier and n-p junction, where n-region is the base⁸ (Figure 1 a). The structure is irradiated by an external light source. The point x_m of the minimum of the potential barrier can be shifted by external voltage U . On the other side the depth in which the light radiation of a certain wavelength can permeate the structure of semiconductor depends on its wavelength giving larger depth for larger wavelengths (see Figure 1b). By changing a voltage U one can detect the sum of spectra observed in a region $x_m - d$ as dependent on x_m and thus on the wavelengths observed. This spectral sum forms a current I . Hence Current-Voltage dependence gives characteristics of the light spectra.

Figure 1. (a) - Double-barrier silicon structure; (b) - The absorption curves of different waves.

To derive the incident light spectra from the Current-Voltage dependence of the diode the following procedure can be used. Current-Voltage characteristics gives measurement data points I_i and U_i , where i changes from 1 to N , covering all the measurement range. Depth for the minimum of the potential is calculated by a formula:

$$x_i = \frac{d}{2} - \frac{\varepsilon_0 \varepsilon (\varphi_2 - \varphi_1 + q U_i)}{q^2 N_d d} \quad (1)$$

where d – thickness of diode zone, ε - relative dielectric permeability, ε_0 – vacuum dielectric permeability, N_d – the concentration of donor impurities, q – electron charge, φ - potential of an electric field, U_i – external Voltage.

In each data point absorption coefficient α_i can be determined as:

$$\alpha_i = \frac{1}{x_i - x_{i+1}} \ln \frac{I_{i+1}}{I_i} \quad (2)$$

And reconstructed radiation flux F_{0i} at a certain point i is:

$$F_{0i} = \frac{I_i - I_{i+1}}{2qS(e^{-\alpha_i x_{i+1}} - e^{-\alpha_i x_i})} \quad (3)$$

Tables can be used to determine what wavelength λ_i corresponds to an absorption coefficient α_i in the specific structure⁹. Hence we get pairs of data points F_{0i} and λ_i , which become the reconstructed spectra of the incident light.

3. EXPERIMENTS

RD Alfa Microelectronics made a design, production and tests of the spectrometer proposed by theory. The proposed structure realized in experiment is given in Figure 2. Diffusion formulas were used to determine necessary condition for the production of the structure – ion alloyage dose (Q), temperature of the process (T), duration of the process (t) for each layer preparation. Conductivity type, material and some characteristics of layers of the diode spectrometer structure are given in Table 1.

Figure 2. Structure of a diode spectrometer.

Table 1. Parameters of layers of a diode spectrometer structure.

No.	Layer	Conductivity type	Material	Layer characteristics
1	Substrate	p	KДБ-12(100)	Thickness $460 \pm 20 \mu\text{m}$
2	Hidden layer	n+	Antimony	Thickness $2.5 \pm 0.25 \mu\text{m}$
3	Hidden layer	p+	Boron trifluoride	Thickness $1,65 \pm 0,25 \mu\text{m}$
4	Epitaxial layer	n	Dichlorosilane Hydrogen chloride	Thickness $5.5 \pm 0.5 \mu\text{m}$
5	Isolation layer	p+	High purity three bromine boron	$D=300 \mu\text{C}/\text{cm}^2$; $E=30 \text{ keV}$
6	n+ protection layer	n	High purity red phosphorus	$D=12 \mu\text{C}/\text{cm}^2$; $E=100 \text{ keV}$
7	p+ protection layer	p	Boron trifluoride	$D=1000 \mu\text{C}/\text{cm}^2$; $E=60 \text{ keV}$
8	Silicide layer		Pt-Si	Thickness $0,07 \pm 0,007 \mu\text{m}$
9	Metalization layer TiW-AlSi		TiW	Thickness $0,12 \pm 0,01 \mu\text{m}$
			AlSi	Thickness $1,4 \pm 0,1 \mu\text{m}$
10	Passive layer		Monosilane concentrate; high purity three oxygen oxide; Refrigerant	Thickness $0,05 \pm 0,005 \mu\text{m}$

The appearance of the chip of the diode is given in Figure 3a. The chip was placed in the shielding, transparent window was added that realize hermeticity of the structure (Figure 3b-3d).

Diode spectrometer chip was irradiated by several light sources: a) blue photodiode (LL-304BC-B4-2BC) with spectral peak at 468 nm and peak width at half maximum 23 nm, b) green photodiode (L-53GC) with spectral peak at 565 nm and peak width at half maximum 30 nm, c) red photodiode (L-813SRC-J4) with spectral peak at 660 nm and peak width at half maximum 20 nm, d) white light photodiode (ll-1003wc-w2-1b), e) xenon lamp (ERNEST LEITZ GmbH Wetzlar; model XBO/CSX) with power 150 W. Current-Voltage characteristics were measured by B2912A Precision Source / Measure Unit with N1295A test fixture (Voltage resolution 1 μV in region $\pm 2 \text{ V}$, with accuracy (% reading + offset) of $\pm(0.02 \%$

+ 350 μ V); Current measurement resolution 100 pA in region $\pm 100 \mu$ A, accuracy (% reading + offset) of $\pm(0.02 \% + 25 \text{ nA})$). Voltage was changed in region - 5 to +5 V with a step 1 mV. Theoretical calculations were used to reconstruct initial spectra from Current-Voltage characteristics.

Figure 3. (a) Diode spectrometer chip, (b-d) chip in the shielding.

4. RESULTS

At first a photo responsiveness of the diode structure was determined. Xenon lamp was used as an initial light source when +5V is set on a diode. A spectral zone of about 6 nm width was cut from xenon spectra by spectrometer Jobin Yvon Triax320 with diffraction grating 600 lines/mm. The central peak of this zone was set to 300, 400, ..., 1100 and 1200 nm and measurements were made. Obtained data are seen in Figure 4. Largest signal was observed at 900 nm position. In this position a Xenon lamp has a peak of an intensity. The responsiveness of 10 - 70 μ A is a good response which shows that the structure works.

Figure 4. Current I for Schottky and p-n diode when irradiated by spectral band cut from Xenon lamp.

The spectrometer diode was irradiated separately by white, blue and red photodiode and Xenon lamp, and Current-Voltage characteristics were observed (Figure 5). The observed current was above 10 μ A for all these light sources when external Voltage of +0.5 V was applied. The largest signal was observed when diode was irradiated by white photodiode. Green photodiode initiated a current of 0.4 μ A on the spectrometer diode when + 0.5 V was applied. Dark current was about 2.2 nA for voltage +0.5 V. Therefore the signal was at least 200 - 5000 times larger than the noise.

Theory was applied to reconstruct initial light spectra. In Figure 6 initial spectra (red) and reconstructed spectra (blue) is given, when structure was irradiated by green photodiode. In Figure 7a-7b we see initial spectra (red) and reconstructed spectra (blue), when structure was irradiated by blue and red photodiodes respectively. Results show that calculations can't reconstruct the shape of an initial spectra, although they reveal signal peaks that corresponds to maximums of initial spectra with about 20 - 30 nm accuracy for green and blue irradiation and about 50 - 100 nm accuracy for red light irradiation.

Figure 5. Current-Voltage characteristics when various light sources are used.

Figure 6. Initial light spectra (red) and reconstructed spectra (blue) when the structure was irradiated by green photodiode.

Figure 7. Initial light spectra (red) and reconstructed spectra (blue) when the structure was irradiated by a) blue photodiode and b) red photodiode.

5. DISCUSSION

5.1 Discussion on accuracy of measurements

Low accuracy of measurements may be the reason for inaccurate reconstruction of measurement data.

Determination of the precision and accuracy of Voltage U. For calculation a case is chosen when $U = + 0.9 \text{ V}$ and green photodiode was irradiated on the spectrometer diode. According to the specification of the apparatus, precision and accuracy of a voltage was $\Delta U \sim (1 \mu\text{V} + 0.02\% \cdot 0.9 + 350 \mu\text{V}) = (1 \mu\text{V} + 180 \mu\text{V} + 350 \mu\text{V}) = 531 \mu\text{V}$ (we estimated that $\Delta U = \text{precision} + \text{accuracy} (\% \text{ reading} + \text{offset})$). In measurements we used voltage step $1000 \mu\text{V}$, which is close to the accuracy of the apparatus. Precision for the determination of α_i is dependent on the precision of $x_i - x_{i+1}$ (see Formula 2). This subtraction is dependent on the precision of Voltage (see Formula 1). Therefore α_i potentially can have large relative error which comes from uncertainty of voltage. This precision can become even $\sim 50\%$ ($= 531 \mu\text{V} / 1000 \mu\text{V}$) if offset is taken into account and $\sim 15\%$ ($= 181 \mu\text{V} / 1000 \mu\text{V}$) when offset is not taken into account.

Determination of the precision and accuracy of current I. For calculation a case is chosen when $U = + 0.9 \text{ V}$ and green photodiode was irradiated on the spectrometer diode. In this case a current was $0.4708 \mu\text{A}$. Measurement accuracy $\Delta I \sim 100 \text{ pA} + (0.02\% \cdot 0.4708 \mu\text{A} + 25 \text{ nA}) = 100 \text{ pA} + 94 \text{ pA} + 2500 \text{ pA} = 0.0027 \mu\text{A}$ (taking into account that $\Delta I = \text{precision} + \text{accuracy} (\% \text{ reading} + \text{offset})$ according to specification of a measurement equipment). Hence relative precision of current is 0.57% . In this region between 2 measurement points I changes about $0.0001 \mu\text{A}$, which is less than the accuracy of measurements. If we use formula:

$$\alpha_i \approx \frac{1}{x_i - x_{i+1}} \frac{\Delta I_i}{I_i} \quad (4)$$

where $\Delta I_i = I_{i+1} - I_i$. We see that precision of α_i depends on the precision of ΔI_i . Hence inaccuracy of measuring I influence α_i substantially. Relative error can reach up to 2700% ($= 0.0027 \mu\text{A} / 0.0001 \mu\text{A}$, if the offset is taken into account) or $100 - 200\%$ ($= 0.000194 \mu\text{A} / 0.0001 \mu\text{A}$, if offset is not taken into account).

It should be concluded that measurement apparatus has large inaccuracy that forms inaccuracy of calculated signals. For better accuracy and precision one should use more precise measurement apparatus.

5.2 Further development of diode spectrometer

Several suggestions have been proposed to increase the performance of spectra reconstruction:

- 1) errors in the reconstructed spectra partially comes from a transmission from coefficient α_i to wavelength λ_i . In calculations table data $\alpha = f(\lambda)$ for silicon was used with λ_i data step 10 nm . More precise tables should be used for better precision. It would be useful to measure absorption coefficient for various wavelengths of the actual structure of diode spectrometer;
- 2) absorption coefficients were determined by using simple formulas (Formulas 1 and 2). For more accurate results transcendental equation should be used for calculations;
- 3) detector structure can be improved by placing connection point of p-n layers deeper in the structure and by effective modulation of barrier widths with external voltage;
- 4) surface barrier has to be transparent for short wavelength – then wavelengths starting from 250 nm can be measured. For this silicide barrier for n base can be used;
- 5) the structure of spectrometer diode has large diffuse regions after base which give large impact on photocurrent from back barrier. This is not welcomed. If oxide layer can be placed after the barrier (back transition) then a large part of wavelengths can go through it without effective generation of photocarrier, which will eliminate diffuse current.

6. CONCLUSIONS

Detector structure was designed to realize a technology of a novel diode spectrometer proposed by theory. The structure was manufactured and tested with various irradiating light sources – white, red, green and blue photodiodes and Xenon lamp. Results show that the structure gives photocurrent that is at least $200 - 5000$ times larger than the dark current. Theoretical manipulations of Current-Voltage dependence give results that can be compared to initial light spectra. The

calculated spectra cannot reconstruct the shape of initial spectra and give the determination of the peak of irradiation spectra with accuracy of about 20 - 100 nm. Accuracy of measurement equipment introduce errors in calculated spectra. Better measurement equipment should be used. Transcendent equations have to be used to obtain better results for reconstructed light spectra. Measurements of absorption coefficient of actual diode structure for various wavelengths are welcomed.

The obtained results show that there are opportunities for the development of novel diode spectrometer, although improvement of measurement setup, the structure of the diode and calculation algorithm should be made.

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