Ultraviolet detectors in thin sputtered ZnO films

Henrik Fabricius, Torben Skettrup, and Paul Bisgaard

Ultraviolet-sensitive photodiodes have been made using the Schottky barrier formed in the contact layer between a thin sputtered layer of ZnO and Au. The sputtering parameters for the ZnO layer were optimized. The IV characteristics and the sensitivity spectra of the ZnO–Au photodiodes were investigated.

I. Introduction

Sputtering of ZnO is a well-known technique.[1–9] The application of sputtered thin films of ZnO has mainly been as surface acoustic wave transducers. To our knowledge nobody has yet used these films as detectors for UV radiation.

Measurements of the intensity of UV radiation, for example in medical applications in connection with UV irradiation of the skin, are very inaccurate due to the lack of suitable detectors in this spectral range.[10] The problem is to sufficiently block out the visible part of the spectrum. To avoid these problems we have in the present work chosen ZnO films which are only sensitive to UV light because the band gap (Eg = 3.2 eV) is in the near-UV spectral range.

ZnO is a material with n-type semiconducting properties.[11] It is so ionic that it cannot be made p-type due to self-compensation effects.[12] Hence, the usual pn photodiodes cannot be fabricated. ZnO photodetectors instead have to be made as either photoconductors or metal–semiconductor junctions (Schottky diodes). Both types of detector have been investigated in this work.

A number of ZnO photoconductors was produced. The photoconducting properties of ZnO are well known.[11,13,14] There exist a fast photoconductive process related to the bulk properties and a slow component related to desorption and adsorption of oxygen atoms on the surface. The fast process is related to and strongly influenced by the slow one.

Paul Bisgaard is with Ferroperm A/S, DK-2950 Vedbaek, Denmark; the other authors are with Technical University of Denmark, Physics Laboratory III, DK-2800 Lyngby, Denmark.

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Our experimental results were in agreement with the above mentioned results. The slow component with decay times of the order of hours implies that this kind of photodetector is unsuitable for practical purposes. Instead we concentrated on the investigations of Schottky diodes on the sputtered thin-film ZnO layers.

II. Sputtering Parameters

The thin-film layers were sputtered on glass substrates in an rf sputtering system with the possibility of biasing the substrate.[15] The target was cast in plaster form from a mixture of 80% burned and 20% unburned ZnO powder. It was then annealed for 4 h at 1000°C. The sputtering parameters were varied systematically to obtain optimum quality of the films [i.e., transparent and nice-looking films with a minimum of internal strain, high values of refractive indices, an absorption edge positioned as far into the UV region as possible, no birefringence (the c axes were always perpendicular to the substrate surface)]. The following parameters were found to be optimal and were applied in the fabrication process. The pressure of the sputtering gas (50% Ar and 50% O_2) was 34–44 mTorr. The target voltage was 700–800 V for zero biasing voltage and 600–700 V when the bias voltage was 0–50 V. With these parameters a typical deposition rate of 300–500 nm/h was obtained.

The sputtered layers were chosen to be 0.5–1 μm thick, since the absorption coefficient of ZnO is of the order of 10^5 cm^{-1}. Their thicknesses and refractive indices were determined from the interference extrema in the transmission spectra. Typical values of refractive indices were 1.89–1.93. (The single crystalline value is 2.0.) The specific resistivities were found to be 0.6–17 kΩ · cm. In Fig. 1 a typical transmission spectrum is shown. The high values of transmission obtained clearly indicate that the optical quality of the film was good. This can also be seen in Fig. 2 where the surface of the film by means of electron microscopy is magnified ~15,000 times. It was found that the size of the surface irregularities is ~60–100 nm, which is much less than the wavelength of the radiation.

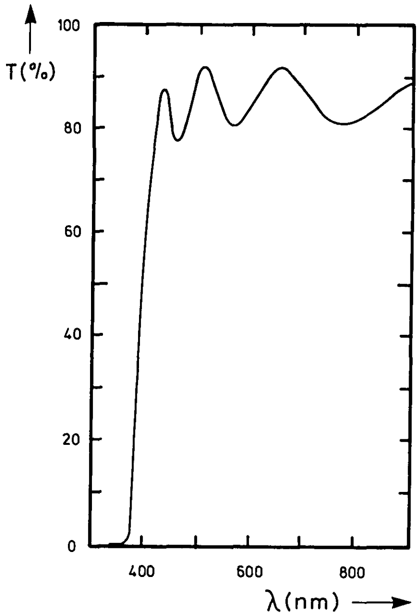

Fig. 1. Typical transmission spectrum of a sputtered ZnO layer.

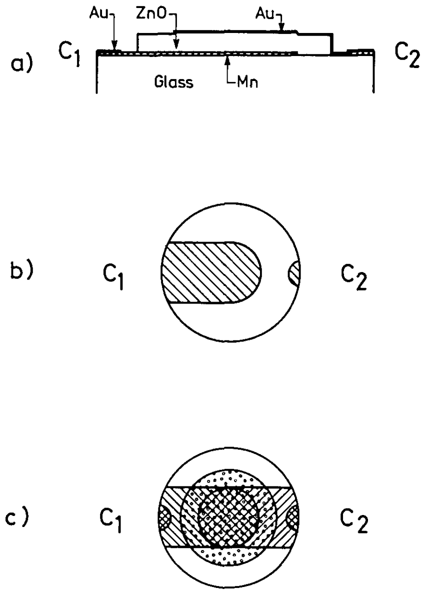

Fig. 3. (a) Design of photodiode; (b) ohmic contact layer on glass substrate; (c) complete photodiode. ZnO layer is dotted while the contact materials are hatched. Wires can be connected to the points C_1 and C_2.

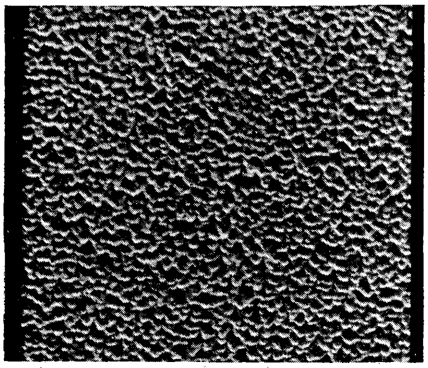
Fig. 2. Surface of ZnO layer magnified ~15,000 times.

III. Schottky Photodiodes

The design of the photodiodes is shown in Fig. 3. A metallic ohmic contact material was evaporated directly on the glass substrate as shown in Fig. 3(b). If necessary a thin binding layer of Cr was also applied between substrate and contact. The ZnO layer was then sputtered on top of this. Finally, a 10–20-nm thick gold layer was evaporated on the structure as seen in Fig. 3(c). With these thicknesses of gold, one obtains a transmission coefficient of ~20%. Gold was chosen because it yields the highest known value for the barrier height between ZnO and metal (0.7 eV).[16] As seen in Figs. 3(b) and (c) it was easy to get electrical contacts to the device at the two gold points C_1 and C_2, which are in direct contact with bottom and top electrodes, respectively. One problem with ZnO is its willingness to give out oxygen. The first diodes had Al as the bottom contact material. However, the Al layer reacted with the ZnO creating an insulating Al_2O_3 layer. It was not possible to get an electrical breakdown in this Al_2O_3 layer without destroying the ZnO–Au barrier. Since an ohmic contact material must be very electropositive to avoid contact barriers,[16] these materials are easily oxidized. Hence it was necessary to choose materials with conducting oxides.

Both In and Zn turned out to be inadequate for the sputtering process, but Mn was suitable, and the manganese oxides are reasonably conductive. Hence the final structure chosen became glass–(Cr)–Mn–ZnO–Au.

IV. Results and Discussion

About 100 diodes were made. Most of them were reasonably good. However, some had a high series resistance probably due to bad contact with the bottom electrode due to the oxide layer, and some had a leakage resistance probably due to badly sputtered ZnO layers with pinholes in the deposited layers.

A typical IV characteristic is shown in Fig. 4 showing the characteristic diode behavior. It is also seen in Fig. 4 that there exists a certain degree of hysteresis in the curves. The origin of this phenomenon has not yet been found.

If the IV characteristic is corrected for contributions from series and leakage resistance, the relationship should be of the usual form

$$I = I_0[\exp(eV/nkT) - 1], \quad (1)$$

where I_0 is the dark current, e is the electronic charge, kT is the thermal energy, while n is a factor accounting for the degree of ideality of the diode. If there are many recombination centers present, n becomes greater than one. In Fig. 5 the corrected curves are shown for several diodes. It is seen that excellent linearity is obtained over several decades in the logarithmic plot

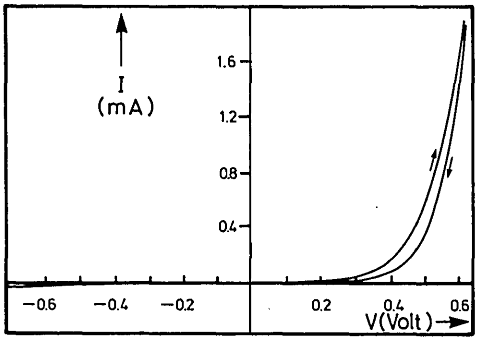

Fig. 4. Typical IV characteristic of a ZnO–Au photodiode.

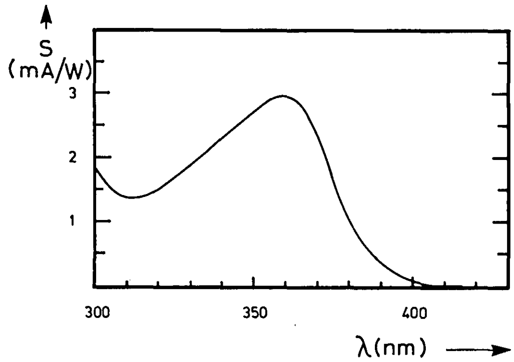

Fig. 6. Sensitivity spectrum of ZnO–Au photodiode.

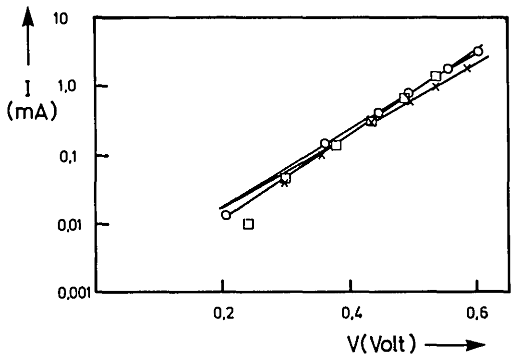

Fig. 5. IV characteristics for three diodes after corrections for series and leakage resistances.

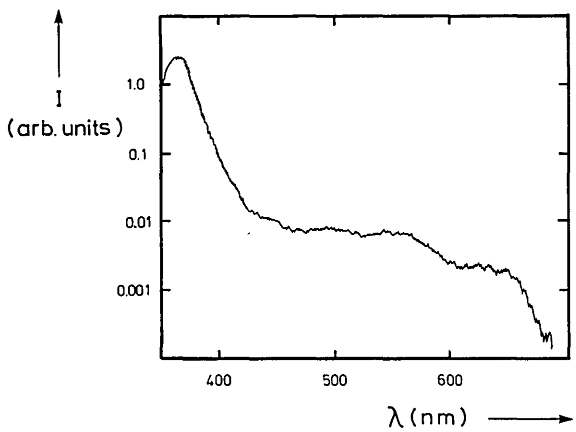

Fig. 7. Sensitivity spectrum of ZnO–Au photodiode in a logarithmic scale.

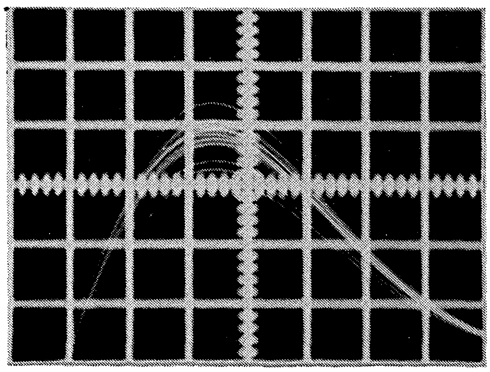

Fig. 8. Typical pulse response of ZnO–Au photodiode illuminated with 7-ns UV pulses from a nitrogen laser. Time scale: 10 μs/div.

in agreement with Eq. (1). The value of I_0 in Fig. 5 was of the order of 40 nA/mm^2. The values of n varied from 2.7 to 3.5. For some diodes, values of n up to seven were found, indicating that this kind of diode structure suffers from severe recombination processes. This is, of course, not surprising since the sputtered ZnO layers are not single-crystalline. These recombination processes also imply a relatively low quantum efficiency of the photodiodes as shown below.

The photoresponse of the ZnO–Au diodes is illustrated in Figs. 6 and 7. In Fig. 6 the sensitivity curve is shown. It is seen that these diodes are sensitive for wavelengths of <400 nm. The absolute value of the sensitivity was found from measurements of the quantum efficiency. The quantum efficiency of these diodes is typical of the order of 1%. This value is relatively low and probably caused by the large amount of recombination centers present as mentioned above. With single-crystalline ZnO layers the quantum efficiency should be considerably improved.

In Fig. 7 the sensitivity curve is shown in a logarithmic scale throughout the visible range of the spectrum. In a Schottky diode there exist a certain photosensitivity for photon energies of less than the band gap energy due to photoexcitation of electrons from the metal contact across the metal–semiconductor barrier. In Fig. 7 it is seen that this sensitivity is several decades less than the band to band response.

The linearity of the response (photocurrent vs intensity of light) was checked at the wavelength of 365 nm by inserting neutral density filters. Over the more than three decades that were investigated, no deviations from linearity were observed.

The pulse response of the diodes was measured by means of the UV pulses from a nitrogen laser with λ = 337 nm and a pulse width of 7 ns. The results are seen in Fig. 8 where a rise time around 20 μs and a decay time of ~30 μs were observed. These relatively long response times seem to be due to the series capacitance and series resistance of the oxide layer in the contact. Values of the order of 0.3 μF and 100 Ω, respectively, can be estimated from an equivalent circuit analysis. Compared with these values the diode capacitance itself of ~10 nF has only little influence on the response times.

V. Conclusions

It has been shown that it is possible to make a UV-sensitive Schottky-barrier diode at the junction between a sputtered ZnO layer and a gold layer. The sputtering parameters were optimized to obtain the most suitable ZnO layers with the highest values of refractive indices. The diode structure consisted of a glass substrate with a Mn electrode as the bottom contact material to the ZnO–Au diode. Mn was chosen because its electronegativity is low and its oxides are conducting. The diodes exhibited conventional IV characteristics. These were influenced by a large amount of recombination centers. The sensitivity and quantum efficiency curves were measured as well as typical rise and decay times. Due to recombination in the polycrystalline ZnO layers and the contact layers the quantum efficiency was of the order of 1%. In a future project we plan to improve this by sputtering epitaxial layers of ZnO at higher temperatures.

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Books *continued from page 2763*

of the nomenclature used in the remainder of the book. Such a summary is fundamental, since workers in the field come from a wide variety of backgrounds. Next, it provides a precis of each computational procedure, including a statement of its advantages and disadvantages. These statements are clearly distillations of the experience of the inventors and advocates of each of the solution techniques, stated in their own words. Thus they contain both quiet advertisements and excuses. The techniques are ordered from the analytic through the detailed numerical to the approximate.

This section also contains a bibliography with references to both the sources of each technique and their practical application. One can trace in this bibliography the sources of a computational method and how the method has fared on different problems. It is clear that for practical computations the matrix operator method and its relative, the adding and doubling method, have more adherents than do other techniques of solving multiple-scattering problems.

The first section closes by presenting a comparison of radiances and fluxes computed by several techniques. This is the heart of the book, and it is interesting to see how the techniques compare (and which did not contribute numbers to the comparison).

The second part is more theoretical, listing various difficult problems, such as radiative transfer in atmospheres with both gas absorption and multiple scattering, in spherical atmospheres, and in horizontally inhomogeneous atmospheres. Again a bibliography is provided.

For anyone wishing to actually compute a multiply scattered radiance, *RADIATIVE TRANSFER*... will probably not be a sufficiently detailed guide to generate a working computer program. However, it is a valuable reference because of the balanced treatment the editor gives to the various techniques of producing numbers for the plane-parallel multiple-scattering problem. Its real triumph is its understated diplomacy and tact, which provides each method of problem solving a reasonable chance for its day in court.

Is radiative transfer dead with this book its obituary? Hardly! It seems more appropriate to regard it as a treaty between the various factions of the atmospheric radiative transfer community, much as the Rosetta Stone was the public record of a treaty in the ancient Middle East. It is hoped it will allow those who sometimes seem to speak in such disparate tongues to reflect on their common progress against a difficult foe.

BRUCE R. BARKSTROM