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Preparation of films based on metal nitrides by the method of magnetron sputtering and study of their optical properties

Abstract: Semiconductor metal nitrides are of considerable interest to researchers due to the possibility of their application. These materials have high radiation, chemical, and thermal resistance and can be widely used to create transparent electronic elements in the future. Due to combining unique optical, electrical, and piezoelectric properties, TiN, CuN, and AgN can be used in sensors, and devices for generating surface acoustic waves, photonic crystals, and LEDs. The study object was thin films of metal nitrides such as TiN, SnN, and AgN, obtained by reactive magnetron sputtering on quartz substrates. The study subject was the optical characteristics of TiN, SnN, and AgN thin films. The study's purpose was to investigate the influence and features of the magnetron sputtering technology on the optical properties of thin films based on metal nitrides deposited by reactive magnetron sputtering. The main methods of this study were the analysis of conditions and technologies for magnetron sputtering of metals in reactive gases and the creation of an improved design of an experimental magnetron for depositing thin films of metal nitrides. Titanium, silver, and tin nitrides (TiN, AgN, SnN) films on quartz substrates were obtained by reactive magnetron sputtering. For this, the authors developed a planetary magnetron on permanent magnets, with an uncompensated magnetic system with a disk cathode. Samples of various configurations of TiN, AgN, and SnN films were obtained. Spectral characteristics of light transmission were investigated for the received samples. The presence of main spectral maxima at 450 and 570 nm was experimentally determined for the studied samples. The physical mechanisms of the existence of these maxima are substantiated. The technology of magnetron sputtering of metals in reaction gas atmospheres has been improved and the possibility of using the obtained films of metal nitrides as optical filters and wide-band semiconductor materials for creating heterojunctions has been substantiated.

Keywords: films of metal nitrides, TiN, SnN, AgN, planetary magnetron, method of reactive magnetron HF sputtering, optical characteristics.

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Отримання плівок на основі нітридів металів методом магнетронного напилення та дослідження їх оптичних властивостей

Анотація: У роботі методом реактивного магнетронного напилення отримано плівки нітридів титану, срібла, олова (TiN, AgN, SnN) на кварцових підкладках. Для цього нами був розроблений планетарний магнетрон на постійних магнітах, з нескомпенсованою магнітною системою з дисковим катодом. Отримані зразки плівок TiN, AgN, SnN різних конфігурацій. Для отриманих зразків досліджені спектральні характеристики пропускання світла. Експериментально встановлено для досліджуваних зразків наявність основних спектральних максимумів 450 та 570 нм. Обгрунтовано фізичні механізми наявності данних максимумів. Вдосконалено технологію магнетронного напилення металів в реакційних газових атмосферах та обгрунтувано можливості використання отриманих плівок нітридів металів в якості оптичних фільтрів та широкозонних напівпровідникових матеріалів для створення гетеропереходів.

Ключові слова: плівки нітридів металів: TiN, SnN, AgN, планетарний магнетрон, метод реактивного магнетронного ВЧ-напилення, оптичні характеристики.

Introduction

The relevance of the research topic. Semiconductor metal nitrides are of considerable interest to researchers due to the possibility of their application (*Musil, 1998*; *Berlin et al., 2007*; *Zhukov et al., 2006*). These materials have high radiation, chemical, and thermal resistance and can be widely used to create transparent electronic elements in the future (*Musil et al., 2007*). Due to combining unique optical, electrical, and piezoelectric properties, TiN, CuN, and AgN can be used in sensors, and devices for generating surface acoustic waves, photonic crystals, and LEDs

(*Musil et al., 2007*; *Nakamura et al., 1994*). Due to their wide band gap, TiN, CuN, and AgN semiconductors can be used as detector materials for detecting ultraviolet radiation (*Nakamura et al., 1994*; *Zhao et al., 2019*; *Northrop…, 2011*). These materials can also create efficient light-emitting diodes (LEDs) and laser diodes. The relatively small discrepancy between the lattice constants of TiN and Si allows them to produce heterojunctions with properties close to ideal (*Chernyaev, 2007*). TiN, CuN, and AgN films also attract the attention of researchers as window, anti-reflective, protective, and current-carrying layers of low-cost, large-area solar cells (*Zhao et al., 2019*).

In the photodetectors and solar cells development, n-TiN/p-Si and n-CuN/p-Si heterojunctions are of particular interest (*Zee, 1988*; *Gotra, 2001*). This is due to the wide photosensitivity region of such structures (560-2000 nm), their low cost, and the availability of hetero-carrier materials.

To obtain thin layers of TiN, CuN, and AgN compounds, such methods as magnetron sputtering, chemical vapour deposition (CVD), and sol-gel methods are widely used today (*Tarui, 2000*; *Ber & Minsker, 2011*). However, wide-bandgap semiconductor compound polycrystalline films' properties obtained by these methods are currently insufficiently studied, hindering the process of their practical use in real devices and elements. This problem determines the choice of the research topic and its relevance. To obtain TiN, SnN, and AgN thin film compounds, reactive magnetron sputtering methods are widely used today.

Magnetron sputtering systems got their name from M-type microwave devices (magnetron devices) although they have nothing in common with them except for the presence of crossed electric and magnetic fields. Magnetron systems are diode-type sputtering systems in which material is atomised by bombarding the target surface with ions of the working gas formed in the glow discharge gas. These systems' high sputtering rate characteristic is achieved by increasing the ion current density due to the localisation of the plasma in the sputtered target surface using a strong transverse magnetic field (*Musil, 1998*; *Zhukov et al., 2006*). Figure 1 shows a classical scheme of a magnetron sputtering system (*Figure 1*).

One of the advantages of magnetron sputtering systems is that the capture of secondary electrons by a magnetic trap near the target surface prevents intense overheating of the substrate. This, in turn, allows for an increase in the rate of sputtering of materials, and hence their deposition. The substrate heating source in these systems is the condensation energy of the sputtered atoms.

It is worth noting that the potential applications of atomisation systems are currently far from being fully understood and realised. They have taken a strong position in the manufacturing semiconductor devices and integrated circuits technology. In particular, they are used to form contacts with various semiconductor and passive circuit elements. They are also used for manufacturing resistive films for hybrid microcircuits, magnetic films, low-impedance contacts, and much more.

In addition, they are widely used in industrial plants for applying thin film coatings. These include various filtering, reflective, protective, and heat-saving optical coatings on glass. Such systems are also widely used in plasma-chemical processing, etching, and material production.

The study object was thin films of metal nitrides such as TiN, SnN, and AgN, obtained by reactive magnetron sputtering on quartz substrates.

The study subject was the optical characteristics of TiN, SnN, and AgN thin films.

The study's purpose was to investigate the influence and features of the magnetron sputtering technology on the optical properties of thin films based on metal nitrides deposited by reactive magnetron sputtering.

The objectives of the study were as follows:

- develop an installation for magnetron sputtering of metals. To obtain thin films of compounds such as TiN, SnN, and AgN by the appropriate method;
- investigate the optical properties of films of compounds such as TiN, SnN, and AgN;
- modernise the spectral complex KSVU-12, to establish its operation using an ADC board.

The main study methods are the analysis of conditions and technologies for metals magnetron sputtering in reactive gases and the creation of an experimental magnetron improved design for depositing thin films of metal nitrides:

- *a method for magnetron sputtering* of thin films of materials in reactive gases (used to produce TiN, SnN, and AgN films);
- *method of measuring spectral characteristics* (used to study the spectral and optical characteristics of thin films of metal nitrides).

The practical significance of the study is that:

1. A magnetron of our design was developed.
2. The spectral complex was modified, its operation in automatic mode, and the processing of experimental data on a computer was provided.
3. New measuring techniques for recording small signal levels using instrumental amplifiers and high-speed ADC board were introduced.
4. The technology of magnetron sputtering of metals in reactive gas atmospheres has been improved, and the possibility of using the obtained compounds as optical filters and wide-bandgap semiconductor materials for creating heterojunctions has been substantiated.

Summary of the main material

The films of metal nitrides (TiN, SnN, AgN) were obtained based on the vacuum universal post-VUP 5M (*Figure 2*).

Sputtering was performed under normal conditions and during the initial holding of the samples in a vacuum (residual pressure in the vacuum chamber was 10^{-5} Pa).

For sputtering, the authors have developed a planetary permanent magnetron with an uncompensated magnetic system together with a disc cathode. The scheme of the magnetron is shown in (*Figure 1*). A photo of the magnetron design is shown in the Appendix (*Figure 3*).

A power supply with a voltage or discharge current stabilisation mode with a maximum power of 1.5 kW was also developed for the magnetron.

Sputtering was performed in a direct current mode.

The authors used silver, titanium and tin as sputtering targets. Sputtering was performed in a nitrogen atmosphere at a chamber pressure of 1-5 Pa (*Figure 4*).

Analysis of the results

Transmittance spectra were studied on the sputtered film obtained samples. The corresponding samples' transmission spectra is shown in the Appendix (*Figure 5*; *Figure 6*; *Figure 7*).

Conclusions

The authors' group has developed an original design magnetron and produced metal films by jet sputtering in a nitrogen atmosphere.

Using a magnetic system with a concentrated field resulted in a high density of ionic currents that sputter the target and, accordingly, a high target sputtering ratio of about 90%. This results in a high productivity of material sputtering.

An installation for magnetron sputtering of materials in a reactive gases' atmosphere has been developed.

The magnetron device design principles make it quite easy to implement the task of applying homogeneous coatings to large-format surfaces and films based on nitrides.

In this work course, AgN, SnN, and TiN films were obtained and their optical characteristics were studied.

As can be seen from the study of spectral characteristics, two spectral maxima of 450 and 570 nm were observed on all samples.

The shorter-wavelength maximum of 450 nm is associated with the vibrations of the nitrogen atom in the studied compounds (AgN, SnN, TiN).

The spectral maximum around 570 nm is due to the vibrational motion of the entire molecule (metal + nitrogen atom).

This theory is also confirmed by the significant intensity of the long-wavelength spectral maximum of TiN since this compound is relatively light compared to AgN and SnN.

The samples studied by the authors open prospects for their use in optics and modern nanotechnology.

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Appendix

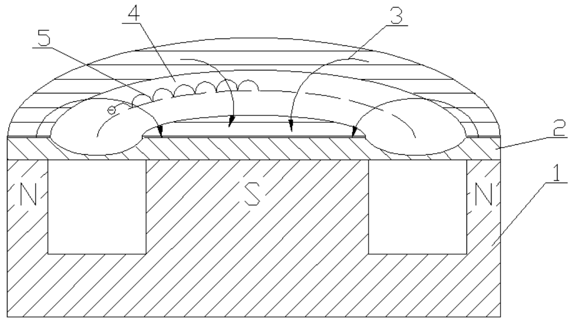

Figure 1. Schematic of a magnetron sputtering system with a flat target: 1 – magnetic system; 2 – cathode-target; 3 – magnetic field line; 4 – zone of the greatest erosion of the cathode surface; 5 – electron trajectory

Figure 2. Photo of the experimental setup

Figure 3. Photo of the developed magnetron

Figure 4. Photo of the spraying process

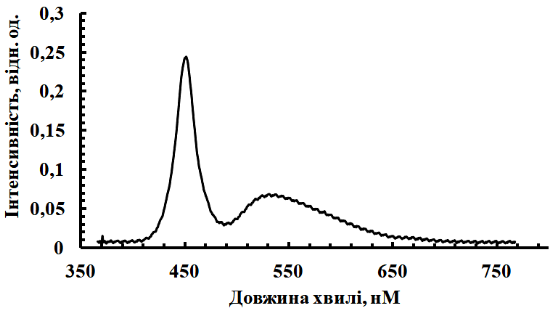

Figure 5. Transmission spectrum of silver nitride (AgN)

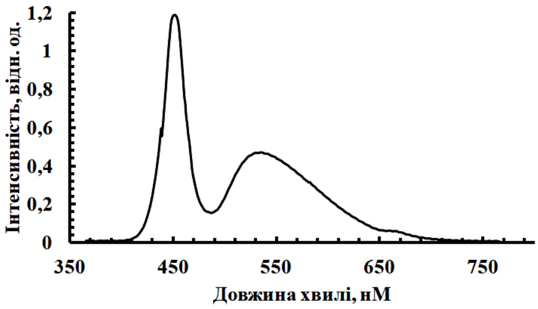

Figure 6. Transmission spectrum of tin nitride (SnN)

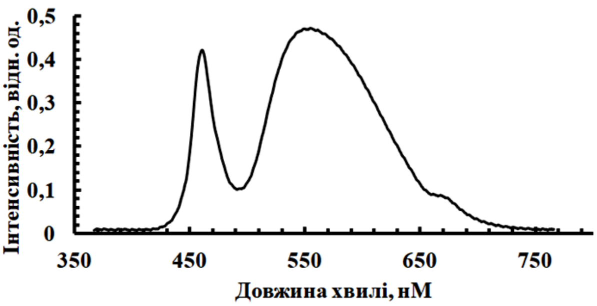

Figure 7. Transmission spectrum of titanium nitride (TiN)