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The influence of copper on zinc oxide properties – a review

E. Chłopocka, E. Nowak

[1] Faculty of Materials Engineering and Technical Physics, Poznan University of Technology, Poland
ewelina.k.nowak@doctorate.put.poznan.pl

ORCID:

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ZnO has been experiencing a research renaissance for several years due to its promising electronics and gas sensing properties. It has a relatively big Eg = 3.37 eV at room temperature, a considerable exciton binding energy (60 meV), and exhibits n-type conductivity. One of the most significant advantages of ZnO is its ability to fine-tuning the conductivity and forbidden energy with doping.

Doping with transition metals can enhance zinc oxide's physical, chemical, and optical properties. One such material is copper, which seems to be an interesting dopant due to its high electric conductivity and similar ionic radii. The possibility of achieving the half-metallic ferromagnetism, p-type conductivity, or shifting the luminescence edge to the blue region seems to be an exciting feature for modern electronics. What is more, Cu doping may increase the thermal resistivity, which can be applied as the material in high-power devices.

The following article consists of a detailed review of studies of copper doped ZnO. The first part of the paper consists of a deep look into the properties of ZnO and the purpose of copper doping of ZnO structures. Due to a wide variety of synthesis methods, the second part consists of studies on the production methods of such structures. The central part of an article is correlated with the studies on structural and optical characterization of Cu doped ZnO; thus, the main body of this paper is divided into three sections. For crystal structure, we derive the analysis of XRD patterns, which gives information on the sub-phases, which may form due to doping. In addition, UV-Vis absorption gives insight into the new material's band structure. Finally, a short section about photoluminescence brings attention to potential applications in LED diodes.

Keywords: crystal structure, doping, photoluminescence.

Вплив міді на властивості оксиду цинку – огляд

Edyta Chłopocka, Ewelina Nowak

Faculty of Materials Engineering and Technical Physics, Poznan University of Technology, Poland

ZnO переживає дослідницький ренесанс протягом декількох років завдяки своїм перспективним властивостям в області електроніки та газодетектування. Він має відносно велику Eg = 3,37 еВ при кімнатній температурі, значну енергію зв'язку екситону (60 меВ) і провідність n-типу. Однією з найважливіших переваг ZnO є його здатність точно регулювати провідність та заборонену енергію за допомогою допіювання.

Допіювання у перехідних металах може посилити фізичні, хімічні та оптичні властивості оксиду цинку. Одним з таких матеріалів є мідь, що виявляється цікавою добавкою завдяки своїй високій електропровідності та подібним іонним радіусам. Можливість досягнення напівметалевого феромагнетизму, провідності p-типу або зміщення краю люмінесценції в область синього спектру виявляється цікавою особливістю для сучасної електроніки. Більш того, допіювання Cu може збільшити тепловий опір, тоді мідь можна застосовувати як матеріал для надпотужних пристроїв.

Ця робота складається з детального огляду досліджень ZnO, допійованого міддю. Перша частина статті складається з глибокого вивчення властивостей ZnO та доцільності допіювання міддю структур з ZnO. Завдяки широкому розмаїттю методів синтезу друга частина складається з досліджень методів виробництва таких структур. Центральна частина статті співвідноситься з дослідженнями структурної та оптичної характеризації ZnO, допійованого Cu; таким чином, основна частина цього документу розділена на три розділи. Для кристалічної структури отримано аналіз зразків рентгенограми, який дає інформацію про субфази, що можуть утворитися внаслідок допіювання. Крім того поглинання у ультрафіолетовому та видимому діапазонах дає змогу зрозуміти зонну структуру нового матеріалу. Нарешті, короткий розділ про фотолюмінесценцію звертає увагу на потенційні можливості використання у світлодіодах.

Ключові слова: кристалічна структура, легування, фотолюмінесценція.

Влияние меди на свойства оксида цинка – обзор

Edyta Chłopocka, Ewelina Nowak

Faculty of Materials Engineering and Technical Physics, Poznan University of Technology, Poland

ZnO переживает исследовательский ренессанс в течение нескольких лет благодаря своим перспективным свойствам в области электроники и газодетекции. Он имеет относительно большую Eg = 3,37 эВ при комнатной температуре, значительную энергию связи экситона (60 мэВ) и проводимость n-типа. Одним из важнейших преимуществ ZnO является его способность точно регулировать проводимость и запрещенную энергию с помощью допирования.

Допирование в переходных металлах может усилить физические, химические и оптические свойства оксида цинка. Одним из таких материалов является медь, которая оказывается интересной добавкой благодаря своей высокой электропроводности и подобным ионным радиусам. Возможность достижения полуметаллического ферромагнетизма, проводимости p-типа или смещения края люминесценции в область синего спектра оказывается интересной особенностью для современной электроники. Более того, допирование Cu может увеличить тепловое сопротивление, тогда медь можно применять в качестве материала для сверхмощных устройств.

Эта работа состоит из детального обзора исследований ZnO, допированного медью. Первая часть статьи состоит из глубокого изучения свойств ZnO и целесообразности допирования медью структур с ZnO. Благодаря широкому разнообразию методов синтеза вторая часть состоит из исследований методов производства таких структур. Центральная часть статьи соотносится с исследованиями структурной и оптической характеризации ZnO, допированных Cu; таким образом, основная часть этого документа разделена на три раздела. Для кристаллической структуры получен анализ образцов рентгенограммы, который дает информацию о субфазах, которые могут образоваться в результате допирования. Кроме того, поглощение в ультрафиолетовом и видимом диапазонах позволяет понять зонную структуру нового материала. Наконец, короткий раздел о фотолюминесценции обращает внимание на потенциальные возможности использования в светодиодах.

Ключевые слова: кристаллическая структура, легирование, фотолюминесценция.

1. Introduction

ZnO is a widely researched material for multiple applications. It is an II-VI compound semiconductor, which due to its native defects, exhibits n-type conductivity. Material has a wide bandgap equal to 3.37 eV and large exciton binding energy (60 meV). Good transparency over a wide range of wavelengths makes it an attractive material for flexible, transparent electronics. ZnO has high electron mobility, exhibits strong photoluminescence at room temperature, and is chemically and thermally stable. The lack of rare earth elements and toxic environmental pollutants makes it an inexpensive and easily disposable material [1]. On top of that, ZnO has piezoelectric properties due to the hexagonal wurtzite structure [2].

Applications of zinc oxide include photocatalysis, solar cells, UV protectors, and gas sensing devices. Moreover, the semiconductor is also considered a potential material candidate for piezoelectric devices [2-3]. ZnO can be found in surface acoustic wave devices, varistors, planar optical waveguides, and ultraviolet photodetectors [3]. Zinc oxide nanoparticles have good biocompatibility to human cells and have been used in the treatment of cancer [1]. From all of the above, gas sensing is incredibly widely researched. ZnO is an n-type semiconductor and, as such, can be used in MOS devices. ZnO can be used as CO [3-5], ethanol [6], and acetone vapor sensor [7].

Doping with transition metals can enhance zinc oxide's physical, chemical, and optical properties. Copper sparks interest as a ZnO dopant due to its high electric conductivity and similar ionic radii [2]. The Cu-doped ZnO exhibits half-metallic ferromagnetism [8]. Cu has been known to cause ZnO emission in the light-blue range when used as a dopant. Cu doping can change the conductivity and visible luminescence in connection with Cu [9].

This paper is an overview of the influence of copper doping on zinc oxide. We undertook this study to bring experimental results from researchers and compare their findings with each other and first-principle calculations [4].

2. Synthesis

На рис. 1 наведені частотні залежності дійсної складової комплексного питомого імпедансу ($ReZ(\omega)$), виміряні в напрямку кристалографічної осі C 5-кратного розширеного Cu doped ZnO can be obtained in a variety of methods. Due to the ease of synthesis, one of the most often chosen synthesis methods is the sol-gel process. The technique allows elaborating a solid material from a solution using a sol or a gel as an intermediate step and at much lower temperatures than traditional preparation methods. The synthesis of solid materials with a sol-gel way often involves wet chemistry reactions and sol-gel chemistry based on the transformation of molecular precursors into an oxide network by hydrolysis and condensation reactions [10]. Due to its advantages, the method was used for the synthesis of Cu-doped ZnO powders [11], thin solid [12], and nanocrystalline [13] films, as well as nanoparticles [7, 14, 15].

Another inexpensive method is the chemical co-precipitation method. Co-precipitation is a phenomenon in which the fractional precipitation of an ion in a solution results in the precipitation of other ions in the solution [16]. In addition, it does not require a high process temperature and is environmentally friendly [2]. This method was used in the synthesis of Cu-doped ZnO nanoparticles [1-3, 16].

Another approach to obtaining doped zinc oxide thin films is the spray pyrolysis technique [5, 6]. In this method of thin-film preparation solution is sprayed on a heated surface, where the constituents react to form a chemical compound.

In many studies, synthesis of Cu-doped ZnO required vacuum. There are reports of thin films deposited by co-sputtering using ZnO and Cu targets [4], pulsed laser deposition [17] and electron beam techniques [17].

3. Crystal structure

Under normal conditions, non-doped ZnO crystallizes in the wurtzite structure with a hexagonal cell; the space symmetry group is (P63mc). Each zinc atom is surrounded by four oxygen atoms located at the corners of a nearly regular tetrahedron [18]. Wurtzite zinc oxide has a hexagonal structure (space group C6mc) with lattice parameters a = 0.3296 and c = 0.52065 nm [19]. The tetrahedral coordination in ZnO results in non-central symmetric structure and consequently piezoelectricity and pyroelectricity. Another important characteristic of ZnO is polar surfaces - the oppositely charged ions produce positively charged Zn-(0001) and negatively charged O-(0001) surfaces, resulting in a normal dipole moment and spontaneous polarization along the c-axis [19]. Many particular features of ZnO are determined by the fact that among the elements of the sixth group, the ionization energy of oxygen is the highest, which leads to a strong interaction between the Zn3d and O2p orbitals [18].

For the influence of Cu doping on ZnO structure, XRD is one of the most used techniques. The crystalline nature of Cu doped ZnO is identical to pure ZnO, even in cases of significant doping in [4], where the atomic ratio of Cu/Zn was as high as 0.38. The peaks can be found around 31.78°, 34.43°, 36.25°, 47.57°, 56.63° and 62.89° which correspond to the Miller Indices (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0) and (1 0 3) [2]. Usually [1-3, 7, 14, 16], the most prominent is the (1 0 1) plane except for study [4], where the thin film had a dominant (002) peak. There are no clear humps that can be unambiguously identified as copper or copper oxides in all cases. It can be concluded that copper is being incorporated into the zinc lattice site rather than at the interstitial position. It is possible and predictable because Cu has similar ionic radii to Zn.

Lattice parameters are stable and equal to about 3.25 Å for a and b constants and 5.20 Å for c constants [1, 2, 20]. Furthermore, [1] explains that the little change in a and c constants does not change the a/c ratio significantly, which stays at 1.60 Å. What does change is the crystalline size in studies on nanoparticles. In [1], crystalline is getting bigger with the increasing content of copper. After further reading, in [2], the grain size is getting minor upon doping under 5% Cu, similar to [16]. Copper concentration above 5% caused the grain size to increase again. These three studies obtained their samples through the chemical co-precipitation method, the only difference being used chemicals.

4. UV-Vis absorption

Researchers agree that Cu doping decreases the optical energy bandgap [1, 2, 20]. Change towards lower energy is to be expected when considering the Cu bulk material band gap equal to 1.4 eV [21]. There can be exceptions to this, for example, being [21] work, where the bandgap increases significantly in Cu doped nanocrystals. The author underlines that this change is anomalous and links it to second-order perturbation theory, which may be more prominent in nanocrystals. On the other hand, it confirms the uniform substitution of Cu ions in the ZnO lattice, as explained in works of [22]. First-principle calculations show that the energy gap can be decreased as much as 0.15 eV by just 6% doping [20]. In the experiment, the most prominent example is [2]'s work, where the bandgap dropped to 2.94eV with 7% wt doping. In comparison, the bandgap in [1]'s study has only decreased to 3.28 eV at 10% doping which shows that lowering the bandgap is not trivial. As mentioned earlier, the crystalline structure is almost identical to that of ZnO. Drop-in bandgap originates not from the structure but many effects taking place like the p–d spin-exchange interactions between the band electrons and the localized d electrons of the transition-metal ion substituting the Cu^{2+} ion., strong p–d mixing of O and Cu, and many-body effects on the conduction and valence bands. Many-body effects shrink the bandgap, which originates from electron interaction and impurity scattering; It has been attributed to the merging of an impurity band into the conduction band and, in the process shrinking the bandgap [2].

5. Photoluminescence

The effects of Cu doping can be seen in PL spectra. ZnO has one peak in the UV region and one in the visible region. Cu doping results in increasing PL intensity of visible region peaks and decreasing UV region peaks simultaneously. An increase in visible region intensity can be linked to defects such as oxygen and zinc vacancies being more prominent in higher doped ZnO [2]. Characteristic green band emission has been reported in numerous articles like [2] and [17]. The latter work is exciting due to the phenomena of green or blue-emitting Cu-doped ZnO depending on the method of fabrication and temperature of annealing. Furthermore, a redshift of spectra has been observed. It is in agreement with previous findings of change in electronic structure; impurity states are created below the conduction band [2].

6. Conclusions

Copper doping enhances ZnO properties. It is the most prominent in PL studies, where copper doping increases light emitted in the visible spectrum. Cu-doped ZnO is a promising material for cost-effective blue, green, and white LED [17].

There is a considerable amount of studies being done on improving gas-sensing properties of ZnO by Cu doping. It has been shown that Cu adsorption is promoted at the Cu sites [4]. Furthermore, copper doping allows zinc oxide to detect ethanol vapors [6], H2, and LPG [3]. UV light illumination on samples caused the detection of acetone and ethanol at room temperature [7]. Studies experimenting with the percentage of doping material and fabrication of samples show that there is much potential in the gas-sensing capabilities of this material.

It is worth mentioning that Cu doping allows keeping the well-known hexagonal wurtzite structure of zinc oxide and at the same time make the material more resistant to high temperatures [1] and lowers its bandgap [1, 2, 20]. First-principle calculations show that introducing copper into the ZnO structure may lead to p-doping [20]. Thus the investigation of the ZnO doped with copper may help create ZnO-based junctions.

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