Recent Progress of β-Ga_2O_3 and Transition Metal doped β-Ga_2O_3 Structure and Properties

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Abstract. Oxide semiconductor material formed from oxygen and a metal is a compound semiconductor material. Important oxide semiconductor materials include Cu_2O, ZnO, SnO_2, Fe_2O_3, TiO_2, ZrO_2, CoO, WO_3, Ga_2O_3 and others. Oxide semiconductors have been receiving strong attention and are widely used in different fields such as solar cells and photovoltaic technology. Due to the development of technology, the high-performance techniques demand more from the parts. Semiconductor is an intensively researched substance that can be used in a wide range of technologies. β-Ga_2O_3 is a metal oxide that has good properties which can fit in different applications. However, due to its wide band gap, it is essentially an insulator. In this case, researchers put a lot of effect into the doping of β- Ga_2O_3 to improve its electronic conductivity. This review summarized the structures and properties of β- Ga_2O_3 single crystal and the amelioration of the characteristics by transition metal (Mn, Zn, V, Fe, Nb, Ta and W) dopants.

Keywords: β-Ga_2O_3, transition metal doped β-Ga_2O_3, semiconducting material.

1. Introduction

Over the years, oxide semiconductors have strongly attracted people's attention and are widely used in different areas such as solar cells, photovoltaic technologies, etc. Among them, Ga2O3 is an oxide material with 5 phases with α, β, γ and δ phases while β-Ga2O3 is the most thermally stable one at high temperatures (above 1000ºC). β-Ga2O3 has been widely used in further optoelectrical applications and power electronics due to its remarkable ultraviolet transmission properties and low cost. The wide band gap makes it an appropriate n-type conductivity semiconductor which is good in UV optoelectronics [1], field effect transistors [2], etc. Like other semiconductors, its properties can be modified or improved by introducing impurities into the lattice to fit different needs in different devices.

The properties of β-Ga2O3 single crystal have been studied such as optoelectronic properties, electrical properties, structural stability under ion irradiation [3], etc. To improve the properties, elements can be doped to adjust the band gap width by introducing an impurity band in the band gap or decreasing the valence band level and/or conduction band level. In recent years many researchers tried to dop elements (Mg, Er, Al, Si, Sn, N, etc) [4-6] into the β-Ga2O3 and deposit on the desired thin film using techniques of MOCVD and MOVPE [7,8], which highly requires the knowledge of the structure and properties of the doped β-Ga2O3. Therefore, the summarization of the recent achievements is necessary and fundamental as the basis for the research. This paper presents the recent advances in the study of β-Ga2O3 single-crystal structure, electronic and optical properties, as well as the effects of transition-metal dopants such as Mn, Zn, V, Fe, Nb, Ta, and W on the structures and properties of β-Ga2O3.

2. β-Ga_2O_3 single crystal structure and properties

With a parameter of a=12.48Å, b=3.09Å, c=5.89Å, and a 103.83-degree β angle, β-Ga_2O_3 has a monoclinic structure and a unit cell with 4 β-Ga2O3 formula units. Ga1 has a tetrahedral geometry while Ga2's is octahedral. For oxygen, O1 is threefold coordinated, one coordinates to Ga1 and two coordinate to Ga2; O2 is fourfold coordinated, sharing three bonds with Ga2 and one with Ga1; O3

is threefold coordinated as well, but has two bonds coordinated to Ga1 and one to Ga2 [9], as shown in fig 1.

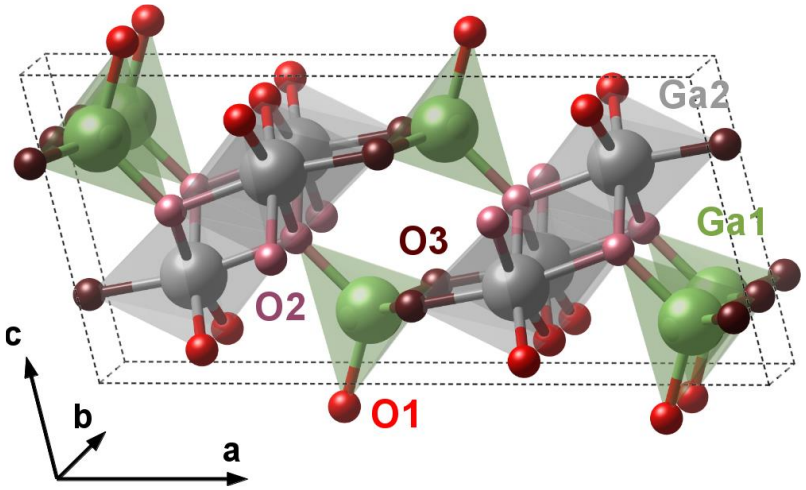

Fig 1. Unit cell of β-Ga2O3 [9].

Ga3+'s electronic configuration which is [Ar] 3d104s04p0, means it is close-shelled as no electron present in the valence band; Oxygen has a $1s^2 2s^2 2p^6$ electron configuration. There is no doubt that Ga-4s is the conduction band while O-2p is the valence band. However, the conduction band is not pure. As O-2p is predominant in the valence band, a hybridization of O-2p and Ga-4s is dominant in the bottom of the conduction band, which is at 2eV above the fermi level [9]. The band gap in β-Ga_2O_3 is wide, which approximately 4.8eV-in UV light energy absorption region, thus it is colorless. In the visible region, the transmittance is more than 90% while in the UV region, it is more than 85% [10].

Because of the wide band gap, a β- Ga_2O_3 with a perfect crystal structure is an insulator(σ=10-9Ω-1cm-1). However, an introduced defect may refine the property as it will become n-type semiconductive. When oxygen is doubly ionized and neighboring Ga3+ is released, deep and shallow donors are formed. The release of Ga ions is different due to the inequivalent of oxygen ions and Ga ions, which produces different formation energy. High temperature is needed in n-type conduction due to the thermal equilibrium of the O1 and O2 vacancy sites which are Evac··=5.2eV and Evac··=4.3eV respectively, while O3 which has a deep-energy gap acts as hole trap[11]. As Ga can be singly ionized or doubly ionized, Ga vacancies are point defects with singly ionized Ga vacancies have a lower formation energy and therefore can form shallow acceptor levels.

P-type conduction is difficult in β-Ga2O3 single crystal because firstly, shallow acceptor states are hard to form is β-Ga2O3, as the valence band weakly interacts purely with O-2p. From the theoretical calculations, the acceptor candidates exhibited to a high activation energy with over 1 eV, which is too high for O-2p. Secondly, the effective hole mass is large and leads to a low diffusion constant which limits the hole conductivity. Lastly, the lattice distortion makes holes that can be recognized as small polarons, which is a hole trap, thus they no longer migrate and conduct electrons. The three factors ensure that p-type conduction is tough, but by creating a built-in potential in the p-n junction, the deep-acceptor doping helps form a large energy barrier [12].

3. Transition metal doped β-Ga_2O_3

3.1. Transition metal doped β-Ga2O3-V to Zn

Transition metal dopants have almost no effect on the lattice structure of β- Ga_2O_3, and the small variations of the lattice parameter are due to the doping ionic radius and coulomb force (repulsion/attraction) will lead to the change of volume of intrinsic β- Ga_2O_3.

As the electronic structure of β- Ga_2O_3 is already discussed, when transition metal is doped, an impurity level may be generated. When Sc is doped, there is no change in the conduction band and

valence band's movements but an impurity level is successfully introduced which makes the band gap narrower, so a better conduction result is achieved. Zn doping has a similar effect, but the impurity level is above the valence band and therefore results in a p-type semi-conductivity. In addition, an increase in atomic number also may influence bandgaps, as from V to Zn doping, the valence band and conduction band gradually move upward while the valence band moves faster thus bandgap is gradually decreasing. The density of the state is calculated and shows more abundant electrons are produced if the d electrons and p-d orbital hybridization are introduced, which can be proved by Fe, Co, Ni and Cu doping. Semiconduction is better to have degenerating in order to improve the ability to conduct electrons. From the Fermi distribution, the impurity concentration has to be between 7.929×1022 and 8.237×1022 cm-3. Optical properties of β- Ga_2O_3 are improved by doping any transition metal dopants, as they all make β- Ga_2O_3 have a red shift.t The higher the atomic number, the more obvious the redshift. This is simply due to the impurity level which is in the middle of the band gap promotes the electronic transition [5].

3.1.1. Mn doped β-Ga2O3

Mn dopant introduced two impurity bands which each contain Mn-3d and neighbor (NN) O-2p orbitals respectively in the bad gap of β- Ga_2O_3 without changing the original band structure. The two impurity bands are either occupied and unoccupied, that is, the occupied one is between the valence band and EF while the other is near the conduction band. To make the impurity bands more delocalized and lower in energy, d-orbitals in Mn split into the impurity bands to culminate it. The vacancy defect helps the valence band edge migrate up, as proved and the minimum transition energy is calculated by Zatsepin et al. [12], Mn dopants a deep donor that donate electrons when EF is lower than 2.78eV, congenitally when EF is higher than 2.78eV, Mn dopants act as acceptors and accept electrons. Because Mn-3d has 6 NN O atoms and Mn-3d orbital is coupled with O-2p orbital, NN O-2p orbitals are polarised which means it contributes unequally to the impurity band. It can be found that the magnetic moment is derived. Different arrangement of O atoms leads to different spinning patterns which induce ferromagnetism and anti-ferromagnetism in the doped compound. Attributed to the strong p-d interaction, and spin-up pattern of O-2p, electrons near EF are active and have a large potential to become free carriers, the ferromagnetic groundwork is able to be maintained no matter how far is between two Mn atoms. As shown by Monte Carlo simulation, when Mn doped into the octahedral Ga atom, the most stable doped system is built with a Tc of 421K, indicating the ferromagnetism can be realized at room temperature [13].

3.1.2. Zn doped β-Ga2O3

As the ion radius of Zn is larger than Ga, the insertion of Zn into β-Ga2O3 will lead to the raise of the lattice constant, confirmed by XRD. Also, from the result of XRD and EDX measurement, Ga sites are replaced by Zn atoms. Since Zn has one electron less than Ga in the outer shell, an acceptor dopant that produces holes is formed by Zn atom, that, Zn doped β-Ga2O3 contributes to p-type conductivity. In CL spectra which is shown in fig. 2, it consists of UV, BL and GL bands at room temperature. The observations reveal that there is a radiative electron transition from donor Vo to valence band, and a donor-acceptor-pair transition is formed from a tunnel recombination of an electron from a donor Vo with a hole from acceptor ZnGa [20]. As Zn dopant concentration increases, the number of holes will increase correspondingly, which means more electrons on donor VO can be recombined [10].

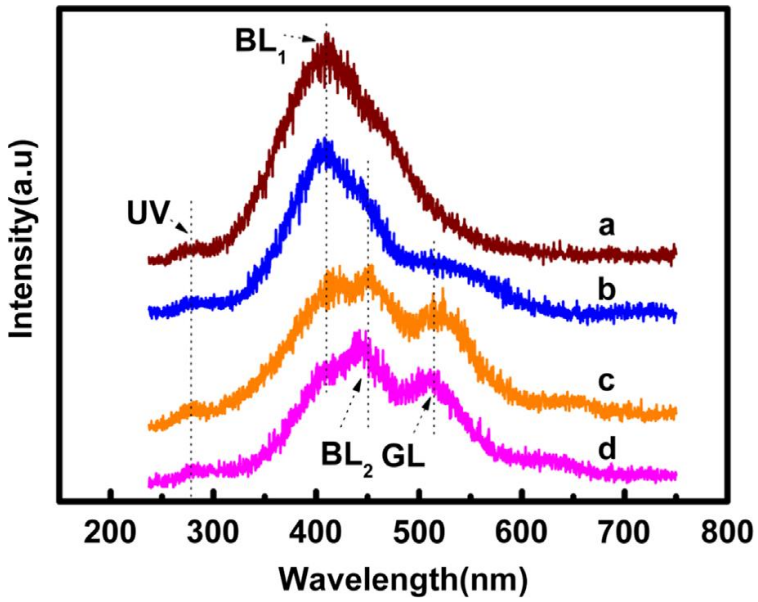

Fig 2. CL spectra of CL spectra of non-doped β-Ga2O3 (curve a) and Zn-doped β-Ga2O3 films with Zn content of 3% (curve b), 5% (curve c) and 7% (curve d) [10]

3.1.3. V-doped β-Ga2O3

V-doped β-Ga2O3 has a monoclinic structure with almost no modification as mentioned above. The carrier concentration is in the range of 1.92×1017 to 4.3×1017 cm-3 which is higher than the doped β-Ga2O3, showing that V atoms can supply free electrons to the β-Ga2O3 substrates which means they act as shallow donors [14]. However, if the V content is too high the excess V will form a cluster on the conduction band which traps electrons, and the carrier concentration will decrease [15]. V atoms tend to occupy the tetrahedral Ga site which is proved by theoretical calculations, the dopants display a large lattice relaxation and trap electrons, which makes them effectively act as deep acceptors. However, from the Raman spectra, V replaces some of the octahedral Ga sites. The highest transmittance of the V-doped β-Ga2O3 is approximately 80% in the visible region, a red shift at the ultraviolet cut-off edge was observed which confirms the optical band gap decreased, attributing to the defect energy caused by increasing V dopant concentration that expands the cluster size [16].

3.1.4. Fe-doped β-Ga2O3

Fe-doped Ga2O3 (GFO) has a more compact structure when the Fe concentration increases as the lattice constant mismatch between intrinsic β-Ga2O3 and GFO raises slightly. The compound has a rod-shaped morphology, and it is monoclinic. In GFO compounds, Fe will substitute the octahedral and tetrahedral Ga sites due to their similar ionic radii and isovalent electron configuration instead of forming intrinsic defects. similarly, Fe can also replace Ga atoms which form interstitial defects. The formation energy is higher when Fe inserts into the octahedral Ga site than the tetrahedral sites [17], and in both configurations, Fe is in deep acceptor level below the conduction band maximum. The confirmed dielectric constant in FGO is mainly created by the polarization that the Fe doping creates, which can be explained by the electrons moving across the ions such as Fe2+, Fe3+, Ga3+ and O2− that produce the local displacement of electrons in the direction of the applied field, thus an orientation polarisation is produced which subsequently increases the dielectric constant. In addition, the charge will accumulate at the grain boundary which increases the interfacial polarization and thus gives help to the rise of the dielectric constant [18].

3.2. Other transition metal doped β-Ga2O3

3.2.1. Nb-doped β-Ga2O3

Nb-doped β-Ga2O3 maintains the monoclinic phase. The lattice constant increases as the dopant concentration increases caused by the ionic radius difference in Ga and Nb as well as the effects of

Coulomb repulsion. The high stability of the doped system is when Ga ion is rich while it has lower formation energy. When the doping concentration climbs, the band gap becomes narrower, and the bond state and anti-bond state have an influence on the valence and conduction bands' moving direction. Ga-4p state and O-2p state which are in the valence band form a bond state, while in the conduction band, Ga-4s and O-2p states form the anti-bond state. When the two states integrate, with a rise in concentration, p-s anti-bonding effect at the bottom of the conduction band is weakened, so the conduction band moves down to a lower energy level. As the p-p bonding effect increases, valence band maximum migrates to the lower energy level. Though the two bands move down, the conduction band minimum migrates more, which results in narrowing the band gap. Deep UV detection can be used to detect the doping concentration level in Nb-doped β-Ga2O3. This is due to the energy required for electrons to jump between two bands decreasing as the band gap is narrowed, thereby the electronic transition is enhanced thus improving the absorption. The optical absorption in the visible region can be seen as due to the transition between impurity energy level and conduction band electrons. Therefore, more doping leads to a higher concentration of conduction band electrons, so better optical absorption performance [19].

3.2.2.Ta doped β-Ga2O3

Ta mainly exists in the β-Ga2O3 lattice as +5 state by XPS measurement. The lattice constant increases as Ta has a larger ionic radius than Ga, confirmed by Raman spectroscopy [20]. After the doping process, the conduction band accepts the electrons from valence band causing a decrease in resistivity from 1.68 to 0.004 Ω cm. Carrier concentration increases from 3.6×1016 to 3×1019 cm-3 and tends to be flat. The electronic mobility decreases from 100 to 50 cm2/Vs. In the visible region, maximum transmittance reaches 80%, and due to the rise in the density of the localised state in conduction band, the optical band gap decreases monotonously. From the Raman spectra, Ta substitutes mainly octahedral sites as the octahedra peaks decrease. The defect levels are analyzed by DLTS and a defect located at 0.73 eV is found under the conduction band [21].

3.2.3.W doped β-Ga2O3

With a formula of Ga2-2xO3-WxO3, W doped β-Ga2O3 (GWO) has a single-phased structure and as W-content rises, the average crystallite size rises. In all GWO compounds, XPS spectra show Ga ion exists in the highest valence states, while a small amount of them is in the lower valence state. In a lower W- concentration compound where x=0.05, the W ion is in a mixture of 4+ and 5+. When x increases further, the W ion in the lower valence state disappears fully, as shown by XRD. W ion dops in the Ga ion sites, whereas, some W ions are in a lower valence state due to the charge imbalance, but they are minor so not expressed in XRD. In general, β-Ga2O3 can only accept a certain concentration of W, but the fully stabilized W-oxide phase evolves as a secondary phase which allows β-Ga2O3 to accept a higher concentration of W and lead to the formation of a composite or mixed oxide [22].

4. Conclusion

Up to now, β-Ga2O3 has been intensively studied and used in different areas. In this review, only the structure and properties of the single lattice and transition metal doped β-Ga2O3 are involved. They are mainly n-type doping as they provide electrons except Zn which is p-type doping. All of them can narrow the band gap of the β-Ga2O3 and make it suitable to be a semiconductor, and the transparency of the doped β-Ga2O3 are high. However, more efforts should be put in to investigate a p-type dopant as the binding energy is lower and the precise control can be carried out.

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