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Modulation of the optical properties of GaN(0001) surface by metal atom adsorption

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Abstract: Based on the first principles study, this paper investigates the control of the optical properties of GaN(0001) surface by metal atoms. The work was conducted with different kinds of metals (Ni, Ru, and Au) that are commonly used in experiments. The results show that charge transfer occurs from adatoms to GaN(0001) surface, and the work function of GaN(0001) surface is reduced by Ni and Ru adsorption. The impurity energy levels are introduced to the band gap of GaN(0001) surface, resulting in the reduction of barrier height of carrier transition, the optical properties are then modulated. The red shift of main peaks in the low photon energy region for all the optical parameters and the shrinkage phenomenon of all the optical curves in the high photon energy region are observed, the numbers and positions of characteristic peaks in all the optical curves change significantly. Furthermore, the absorption of GaN(0001) surface to visible light and even infrared light is enhanced after the adsorption of metal atoms, which is suitable for the longer wave light detection instead of UV detection.

Key words: GaN(0001) surface, metal atom adsorption, first principles study, optical properties
PACS: 73.20.-r, 73.20.At, 73.20.Hb, 78.20.-e, 78.20.Ci, 78.67.-n, 78.67.Pt

金属原子吸附对GaN(0001)表面光学性能的调制

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摘要:基于第一性原理计算,研究了实验中常用的金属(Ni、Ru和Au)等三种原子对GaN(0001)表面光学性质的调控。结果表明,电子从吸附原子中转移到GaN(0001)表面,Ni和Ru的吸附降低了GaN(0001)表面的功函数。在GaN(0001)表面的带隙中引入了杂质能级,使载流子跃迁的势垒高度降低,进而调节其光学性 。可以看到在低光子能量区所有光学曲线的主峰红移,而在高光子能量区所有光学曲线都出现收缩现象,所有光学曲线上特征峰的数量和位置都发生了明显的变化。此外,吸附金属原子后,GaN(0001)表面对可见光甚至红外光的吸收增强了,适用于较长波光的探测。

关 键 词:GaN(0001)表面;金属原子吸附;第一性原理计算;光学性能
中图分类号:O469　　**文献标识码**:A

Introduction

GaN material occupies an important position in modern electronic and optoelectronic devices due to its advantages such as wide bandgap, excellent transmission characteristics, and the wavelength range from near infrared band to near ultraviolet band. GaN has low electron affinity, which can be used as field emission electron source. GaN based blue and green LED (light-emitting diode) and laser diode can be realized due to its wide direct bandgap[1-14]. The work function of GaN can be reduced by covering Cs and O, so as to obtain photocathode, which can be used to prepare vacuum photoelectric devices such as vacuum electron source and ultraviolet detector[15-20]. GaN has many different surfaces, different types of GaN surfaces tend to exhibit different characteristics. There are unsaturated suspension bonds on the polar sur-

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face of GaN(0001), which will produce surface states in the band gap, thus making GaN surface show different characteristics. The surface states in the energy band gap of the GaN (0001) surface will be significantly changed by doping metal atoms, so as to regulate the photoelectric properties of the GaN(0001) surface.

Substitutional doping has been widely used to modulate the properties of GaN. For example, GaN exhibits p-type semiconductor characteristics by Be or Mg doping, and GaN exhibits n-type semiconductor characteristics by Si doping[21-25]. Ji *et al.* investigated the photoelectric properties of GaN surface doped with Si, the weak absorption and reflection of ultraviolet light by GaN are observed, which can be used for ultraviolet light detection[26]. Svane *et al.* studied the electronic structure of cubic GaN doped with rare earth atoms [27]. Sanna *et al.* studied the defect pairs associated with rare earth atom (Eu, Er, Tm) doping in GaN, which can be concluded that rare earth elements have a strong selectivity for Ga lattice sites[28]. Adsorption doping is another way to effectively modulate the properties of GaN. For example, the adsorption of alkali metals can affect the work function and band structure of GaN, thereby modulating its electronic and optical properties [29-33]. Xia *et al.* studied the adsorption of Cs on the surface of GaN nanowires[001], the work function of GaN nanowires is greatly reduced[34]. Beimaskaya *et al.* reported that photoemission of Cs/GaN(0001) n-type interface can be observed by exciting visible light in GaN transparent region [35].

In this study, different metals (Ni, Ru, and Au) that are commonly used in experiments are selected to adsorb on the GaN(0001) surface to tune its photoelectric properties through the first principles calculation. The optical properties have been investigated through the hybridization of electronic states and the electron transition theory. Collectively, the results may well provide an especially useful framework for the application of GaN(0001) surface in optoelectronic field.

1 Computational detail

In this paper, the Cambridge Sequential Total Energy Package (CASTEP) module is adopted to calculate the electronic structure, work function, and optical properties of metal atom adsorbed GaN(0001). Simulations are performed under generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange and correlation. In the process of structure optimization, 450eV mesh cutoff energy is set for the expansion of plane wave basis sets and the convergence criteria is set to 5×10^{-6} eV for all systems. The Brillouin-zone (BZ) integration is calculated by the highly symmetric K points in the form of a Monkhorst-Pack 9×9×1 grid. The convergence criterion of the interaction force between atoms is set to 0.02 eV, and the stress convergence criterion in the crystal is set to 0.1 GPa. The convergence criterion of the maximal displacement of atoms is 1×10^{-3} Å. All calculations are carried in reciprocal space with Ga $4s^24p^1$, N $2s^22p^3$, Ni $3d^84s^2$, Ru $4d^75s^1$, and Au $5d^{10}6s^1$ as the valence electrons.

2 Results and discussion

A 4×4×3 supercell of the GaN(0001) surface structure is constructed as shown in Fig. 1(a), the top two layers of this model are relaxed freely, the bottom four layers are fixed. 30 Å vacuum region perpendicular to the GaN(0001) surface is added, which is verified to be wide enough (based on the average electrostatic potential plot). The boundary conditions are set to be periodic. For the GaN(0001) surface, the hollow sites (at the center of a hexagon), the top of gallium atom, the top of nitride atom, and the center of bridge between gallium and nitride atoms are the possible adsorption sites. The GaN (0001) surface structures with adatoms occupying different adsorption sites are optimized, the results show that the adatoms prefer to occupy the hollow site of the GaN (0001) surface. Thus, the following discussions are all with respect to the GaN(0001) surface structure with adatoms occupying hollow adsorption site as shown in Fig. 1(b).

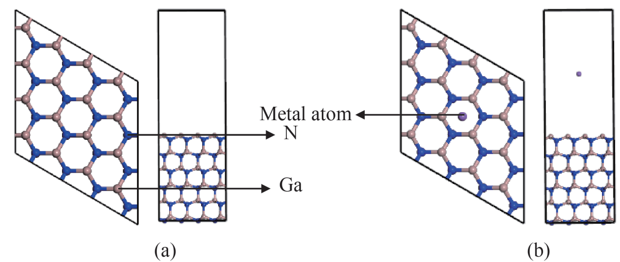

Fig. 1 The 4×4×3 structures of (a) pristine GaN(0001) surface, and (b) GaN(0001) surface adsorbed with metal atom. (Adatoms occupy the center of the hexagon)
图1 4×4×3 GaN(0001)表面的(a)本征结构和(b)吸附金属原子的结构(吸附原子占据六角的中心)

For the GaN (0001) surface adsorbed with metal atom, the vertical distance between the adatom and the GaN (0001) surface is an important parameter. When the vertical distance between the adatom and the GaN (0001) surface is much longer than the bond length between N and Ga, there is no interaction between the adatom and the GaN(0001) surface. The vertical distance between the atoms and the GaN(0001) surface is less than the bond length between N and Ga, the bond length between N and Ga below the adatom increases as the adsorption distance decreases, the interaction between adatom and GaN (0001) surface is enhanced so that more charges transfer between them, the strength of orbital hybridization at the Fermi level of the GaN(0001) surface is enhanced at the same time. When the vertical distance between the adatom and the GaN (0001) surface is much smaller than the bond length between the N and Ga, the adatom will be transferred to the GaN(0001) surface, thus the GaN(0001) surface structure is destroyed. Taking the above results into consideration, the vertical distance between adatoms and the GaN (0001) surface is set to 2 nm.

The binding energy of atoms adsorbed on the GaN (0001) surface can be defined as:

$$E_b = \frac{E_{GaN-nM} - E_{GaN} - nE_M}{n} \quad , \quad (1)$$

where E_{GaN-nM} is the total energy of the GaN(0001) surface adsorbed with metal atoms, E_{GaN} is the total energy of the GaN(0001) surface, E_M is the total energy of the free metal adatom, and n corresponds to the number of metal adatoms. The calculated binding energies of atoms adsorbed on the GaN(0001) surface are shown in Table 1. It is seen that all the binding energies of these adatoms are negative, indicating that these adsorption processes are exothermic, and the adsorption structures are stable. These results are like to those of adsorption structures of the GaN film presented in Ref. 36. The ionization potential is one of the most important factors that determine the binding energy of atom adsorbed on the GaN(0001) surface. The larger ionization potential of metal atom corresponds to the larger absolute value of the binding energy of atom adsorbed on the GaN(0001) surface. Among the three adatoms, Ni has the largest ionization potential and corresponds to the largest absolute value of the binding energy.

Table 1 Binding energies of atoms adsorbed on the GaN(0001) surface (E_b in eV)

表1 GaN(0001)表面吸附原子的结合能(E_b/eV)

Adatom	Ni	Ru	Au
Binding energy (E_b/eV)	−84.4	−80.0.6	−82.2

Charge transfer is another important feature in the adsorption process. The number of transferred charges is presented in Table 2. As seen, all the adatoms loss the electrons due to the fact that their electronegativity is smaller than that of Ga atom. In the case of the GaN(0001) surface adsorbed with Ni and Ru, relatively notable electrons transfer from adatoms to GaN(0001) surface, suggesting significant chemical interaction between the adatoms and the GaN(0001) surfaces. For the GaN(0001) surface adsorbed with Au, small number of charges transfer from adatoms to GaN(0001) surface, which implies that weak interactions occur between adatoms and the GaN(0001) surface. The large charge transfer corresponds to strong interactions between the adatoms and the GaN(0001) surface, resulting in strong orbital hybridization between the adatoms and the GaN(0001) surfaces at the Fermi level, thus the work function of the GaN(0001) surface can be reduced.

Figure 2(a) shows the energy band structure of the pristine GaN(0001) surface. The direct band gap of the pristine GaN(0001) surface is observed, as well as the conduction band minimum (CBM) and the valence band maximum (VBM) locate at the G point in the Brillouin zone; the band gap E_g is 2.217eV, corresponding to the results shown in Ref. 37. Figures 2(b-d) show the energy band structures of the GaN(0001) surface adsorbed with different metal atoms. In the case of the GaN(0001) surface adsorbed with Ni, the direct but significantly reduced band gap is observed, the band gap is 0.32 eV. Some impurity energy levels below the Fermi level in the band gap are introduced, the smaller energy difference between impurity energy levels, impurity energy level and CBM, impurity energy level and VBM are also observed. The case of the GaN(0001) surface adsorbed with Ru is similar to that of the GaN(0001) surface adsorbed with Ni, the band gap is 0.001 eV, some impurity energy levels below and above the Fermi level in the band gap are observed. For the GaN(0001) surface adsorbed with Au, an impurity energy level that passes through the Fermi level is observed. The energy difference between impurity energy level and CBM (VBM) is 2.26 eV (0.15 eV), which is smaller than the band gap of pristine GaN(0001) surface. The reduction of energy difference between energy levels due to the adsorption of metal atoms on the GaN(0001) surface reduces the barrier height of carrier transition and facilitates the interband transition.

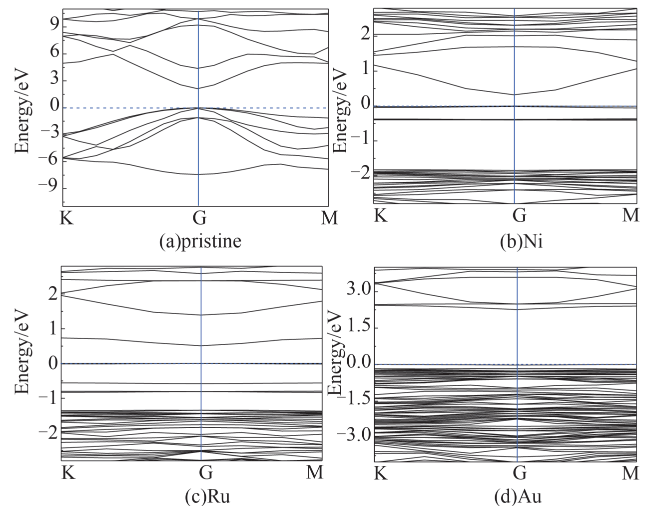

Fig. 2 Energy band structures of (a) pristine GaN(0001) surface, and(b-d) GaN(0001) surface absorbed with different metal atoms. The blue solid lines represent G point of the Brillouin zone, the blue dashed line at 0 eV represents the Fermi level

图2 (a)本征GaN(0001)表面以及(b-d)GaN(0001)表面吸附不同金属原子的能带结构。蓝色的实线代表布里渊区的G点，0 eV处的蓝色虚线代表费米能级

Table 2 Number of transferred charges between the adatoms and GaN(0001) surface. Positive values represent that charges transfer from adatoms to GaN(0001) surface

表2 GaN(0001)表面和吸附原子之间转移的电荷数。正值代表电荷从吸附的原子转移到GaN(0001)表面中

Adatoms	Ni	Ru	Au
Number of transferred charges	0.27	0.26	0.05

Figure 3 shows the partial density of states (PDOS) of the pristine GaN(0001) surface and GaN(0001) surface adsorbed with different metal atoms. From Fig. 3(a) we can see that the valence band of pristine GaN(0001) surface is divided into the upper valence band and the lower valence band from left to right, the Fermi level is located at the edge of the upper valence band. From

Figs. 3 (b-d) we can see that orbital hybridization between adatoms and GaN(0001) surface at the Fermi levels takes place, the types of orbitals involved in hybridization and the intensity of orbital hybridization vary due to the adsorption of different metal atoms on the GaN(0001) surface. Charges transfer occurs between adatoms and GaN(0001) surface simultaneously, all the adatoms loss electrons due to their smaller ionization potential than that of Ga atom. In the case of the GaN(0001) surface adsorbed with Ni, strong orbital hybridization takes place between the 3*d* state orbits of Ni and the 2*p* states orbits of N at the Fermi level, 0.27 electrons transfer from the 3*d* state orbits of Ni to the GaN(0001) surface. In the case of the GaN(0001) surface adsorbed with Ru, strong orbital hybridization between the 4*d* state orbits of Ru and the 2*p* state orbits of N at the Fermi level also is observed, 0.26 electrons transfer from the 4*d* state orbits of Ru to the GaN(0001) surface. For the GaN(0001) surface adsorbed with Au, weak orbital hybridization takes place between the 6*s* state orbits of Au and the 2*p* state orbits of N at the Fermi level, 0.05 electrons transfer from the 6*s* state orbits of Au to the GaN(0001) surface. The strength of orbital hybridization between adatoms and the GaN(0001) surface represents the chemical interaction between them, the work function of GaN(0001) surface can be reduced by stronger orbital hybridization.

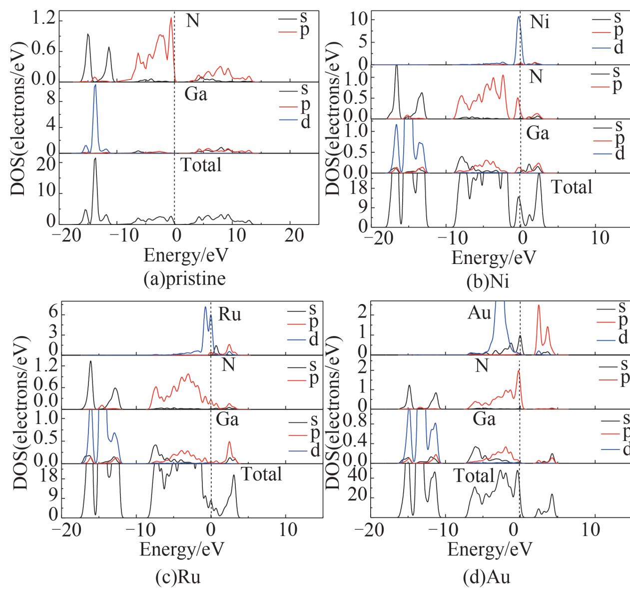

Fig. 3 PDOS of (a) pristine GaN(0001) surface, and (b-d) GaN(0001) surface absorbed with different metal atoms. The dashed line at 0 eV represents the Fermi level
图3 (a)本征GaN(0001)表面以及(b-d)GaN(0001)表面吸附不同金属原子的分波态密度。0 eV处的虚线代表费米能级

The work function (Φ) is an important parameter to determine the photoelectric properties of materials. Lower work function can improve the photoelectric properties of materials to some extent. The work function of any material can be defined as the energy required to remove an electron from the highest filled level in the Fermi distribution of a solid to vacuum at absolute zero. The calculated Φ of the pristine GaN(0001) surface is 4.483eV, which is in good agreement with the experimental value of (4.0 ± 0.2) eV [38] and close to the calculated result of 4.42 eV in Ref. 39. The work functions of the GaN(0001) surface adsorbed with different adatoms are 3.43 eV (Ni), 3.77 eV (Ru), and 5.29 eV (Au) respectively. It is seen that some metal atoms adsorption can reduce the work function of GaN(0001) surface while other metal atoms adsorption cannot. The increase or decrease of the work function of GaN(0001) surface depends on the electronegativity of the adatoms with respect to the Ga atom. In the case of the GaN(0001) surfaces adsorbed with Ni and Ru, the electronegativity of the adatoms is smaller than that of Ga atom. The surface dipole moment will be formed due to the interaction between adatoms and GaN(0001) surface, which reduces the work function of GaN(0001) surface. For the GaN(0001) surfaces adsorbed with Au, the work function is bigger than that of pristine GaN(0001) surface due to the bigger electronegativity of Au atom. Furthermore, the strength of orbital hybridization between adatoms and GaN(0001) surface at the Fermi levels has an indirect influence on the reduction of work function of GaN(0001) surface. From the analysis of PDOS of GaN(0001) surface adsorbed with metal atoms above we know that strong orbital hybridization takes place between Ni or Ru and the GaN(0001) surface at the Fermi level, which corresponds to the smaller work function of GaN(0001) surface.

The optical constants, relating the microscopic model of physical process with the microelectronic structure of the solid that can better characterize the physical properties of the material, are mainly determined by the electronic structures and the carrier concentration near the Fermi level. The changes of the electronic structures of GaN(0001) surface caused by the adsorption of different metal atoms would influence its optical properties. Figures 4(a-b) represent the frequency dependent real and imaginary parts of dielectric function $\varepsilon(\omega)$ of the pristine GaN(0001) surface and the GaN(0001) surface adsorbed with different metal atoms. $\varepsilon_1(\omega)$ represents the real part of dielectric function, $\varepsilon_2(\omega)$ represents the imaginary part of dielectric function. For the pristine GaN(0001) surface, the static dielectric function $\varepsilon_1(0)$ is found to be 3.44, six main peaks are observed in the graph of $\varepsilon_2(\omega)$ at photon energy of 2.29 eV, 6.84 eV, 8.85 eV, 10.82 eV, 13.13 eV, and 17.51 eV. The peak at 2.29 eV corresponds to the transition of carriers from N 2*p* state orbit at VBM to Ga 4*s* state orbit or Ga 4*p* state orbit at CBM; the peak at 6.84 eV indicates the transition of carriers from Ga 4*s* state orbit within the upper valence band to Ga 4*p* state orbit within the conduction band; the peak at 8.56eV indicates the transitions of carriers from N 2*p* state orbit within the upper valence band to Ga 4*s* state orbit or Ga 4*p* state orbit within the conduction band; the peak at 10.82 eV corresponds to the transitions of carriers from Ga 3*d* state orbit within the lower valence band to N 2*p* state orbit within the upper valence band; the peak at 13.13 eV corresponds to the transitions of N 2*s* state (lower valence band) to N 2*p*

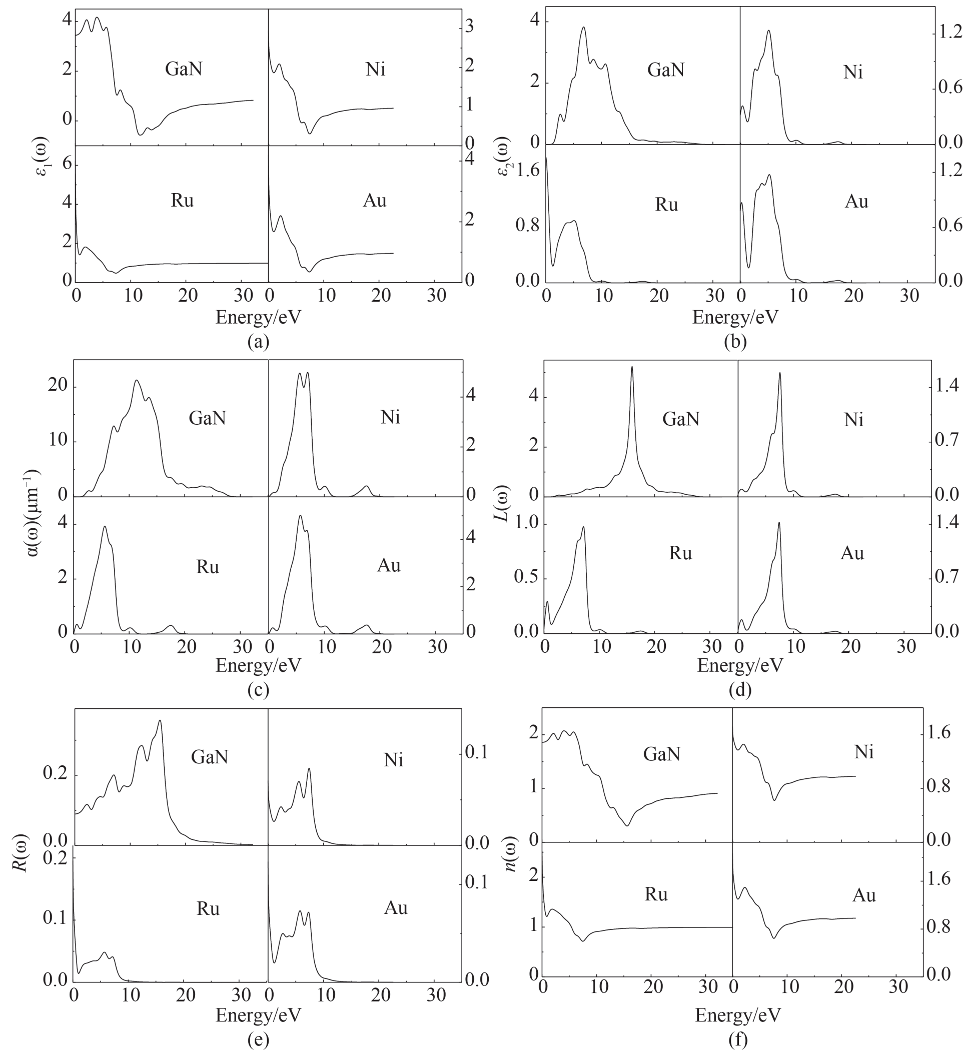

Fig. 4　Optical properties of GaN(0001) surface absorbed with different metal atoms (a) real part of dielectric function, (b) imaginary part of dielectric function, (c) absorption, (d) loss function, (e) reflectivity, and (f) real part of refractive index

图4　GaN(0001)表面吸附不同金属原子的光学性能 (a)介电函数的实部,(b)介电函数的虚部,(c)吸收率,(d)损失函数,(e)反射率,(f)折射率的实部

state (upper valence band); the peak at 17.51 eV corresponds to the transitions of carriers from N 2*s* state orbit within the lower valence band to Ga 4*s* state orbit or Ga 4*p* state orbit within the conduction band. In the case of the GaN (0001) surface adsorbed with Ni, $\varepsilon_1(0)$ is found to be 2.94, which is smaller than that of pristine GaN(0001) surface. In the case of the GaN(0001) surfaces adsorbed with Ru and Au, $\varepsilon_1(0)$ is found to be 6.25 and 4.21 respectively, which are bigger than that of pristine GaN(0001) surface. From Fig. 4(b) we can see that the numbers and the positions of the peaks in $\varepsilon_2(\omega)$ that represent the transition of carriers change significantly. The peaks at 0 eV in $\varepsilon_2(\omega)$ for all the GaN (0001) surfaces adsorbed with different metal atoms are observed, which represent the orbital hybridization between adatoms and GaN (0001) surface at the Fermi levels. Two peaks close to each other in the lower photon energy region are also observed, which correspond to the transitions of carriers between Ni 3*d*, Ru 4*d*, and Au 6*s* state orbits and Ga 4*p*, N 2*p* state orbits.

Figure 4(c) shows the absorption coefficients of the pristine GaN(0001) surface and the GaN(0001) surface adsorbed with different metal atoms. For the pristine GaN (0001) surface, the maximum value of the absorption coefficient is 21.3 μm^{-1} at the photon energy of 10.82 eV. The absorption edge begins at the photon energy of 2.29 eV, which corresponds to the direct transition threshold of carriers (VBM to CBM) and is in agreement with Ref. 40. For the GaN(0001) surface adsorbed with different metal atoms, the absorption intensity of light has changed a lot; the shrinkage phenomenon of the absorption curve in the high photon energy region is observed, indicating the weak absorption of high frequency electromagnetic wave. The optical range of the absorption spectra is separated into two parts, red shift of the absorption peaks in the lower photon energy region is observed. From Fig. 4(c) we can see that the absorption spectrum covers the entire visible light region, and a new absorption peak appears in the infrared region below the visible

light.

The electron energy loss spectrum (EELS) is defined as the amount of energy that an electron loses when it passes through a single medium. EELS describe the energy loss of electrons in a homogeneous medium. The peak value of EELS represents plasma turbulence, and the corresponding oscillation frequency is known as the plasma frequency. A single sharp peak of height 5.2 in the EELS is observed at 15.9 eV for the pristine GaN (0001) surface, corresponding to the transitions of carriers from N 2*s* state orbit within the valence band to orbit at CBM. The position of this peak represents the edge energy of plasma and indicates the transition point of the GaN(0001) surface from metallic properties to dielectric properties. For the GaN (0001) surface adsorbed with different metal atoms, a broaden main peak of EELS is observed, indicating the existence of other transition peaks of carriers near the edge peak of plasma. The height of the main peak is significantly reduced, indicating the reduction of plasma oscillations intensity; the position corresponding to the main peak of EELS shifts towards the direction of low photon energy region, indicating the reduction in transition height of carriers due to the existence of the impurity energy level in the band gap of the GaN(0001) surface. Furthermore, a new smaller plasma excitation peak in the photon energy region below the visible light region is observed, which corresponds to the transitions of carriers from impurity energy level (Ni 3*d* state orbit, Ru 4*d* state orbit, and Au 6*s* state orbit) to CBM or VBM.

There is a correlation between EELS and reflectivity $R(\omega)$, the peak of EELS corresponds to the sharp drop in the reflectivity curve. For the pristine GaN(0001) surface, the maximum reflectivity is 0.36 at the photon energy of 15.4 eV. A lot of reflection peaks in the photon energy range from 0 eV to 15.4 eV are observed, the reflectivity curve drops sharply over the photon energy range of 15.4 eV until 0 eV. For the GaN(0001) surface adsorbed with different metal atoms, the shrinkage phenomenon of the reflectivity curve in the high photon energy region is observed. The maximum reflectivity decreases dramatically, the position corresponding to maximum reflectivity peak shifts toward the direction of low photon energy region, and the number of reflectivity peaks decreases greatly. A slightly larger reflectivity peak at the 0 eV is observed, corresponding to the reflection of hybridization energy level due to the orbital hybridization between the GaN(0001) surface and adatoms at the Fermi level.

The optical parameter corresponding to the reflectivity is the refractive index. Figure 4(f) shows the real part of the refractive index $n(\omega)$ of the pristine GaN (0001) surface and the GaN (0001) surface adsorbed with different metal atoms. For the pristine GaN(0001) surface, the static value of refractive index $n(0)$ is 1.86, the maximum $n(\omega)$ is 2.07 at the photon energy of 4.02 eV. The absorption of the high frequency electromagnetic wave decreases with increase in the photon energy above 20 eV, and the change in the refractive index curve is observed to be very small. For the GaN(0001) surface adsorbed with different metal atoms, the shrinkage phenomenon of the $n(\omega)$ curve in the high photon energy region is observed.

The maximum $n(\omega)$ decreased to some extent, the position corresponding to maximum refraction peak shifts toward the direction of low photon energy region, and the number of refraction peaks in the curve decreases significantly. Furthermore, the refraction peak corresponding to the maximum refractive index appears at 0 eV, which is closely related to orbital hybridization between the GaN (0001) surface and adatoms at the Fermi level.

Table 3 Key parameters of the pristine GaN(0001) surface and the GaN(0001) surface adsorbed with different metal atoms

表3 本征GaN(0001)表面和吸附不同金属原子的GaN(0001)表面的关键参数

	Pristine structure	Adsorption structure		
	GaN(0001)	GaN (0001)-Ni	GaN (0001)-Ru	GaN (0001)-Au
E_g/eV	2.217	0.32	0.001	-
Φ/eV	4.42	3.43	3.77	5.29
$\varepsilon_1(0)$	3.44	2.94	6.25	4.21
$\alpha(\omega)_{max}/\mu m^{-1}$	21.30	4.99	3.93	5.03
$L(\omega)_{max}$	5.20	1.59	0.98	1.43
$R(\omega)_{max}$	0.36	0.085	0.2	0.12
$n(\omega)_{max}$	2.07	1.72	2.52	2.06

3 Conclusions

In summary, some metals that are commonly used in experiments (Ni, Ru, and Au) are adopted to tune the work function and optical properties of GaN (0001) surface through the first principle calculations. Based on the analysis of orbital hybridization and carrier transitions in the energy band structures and PDOS, the modulation mechanisms of optical properties of GaN (0001) surface by metal atoms adsorption are well understood. Some key parameters of the pristine GaN(0001) surface and the GaN(0001) surface adsorbed with different metal atoms are shown in Table 3. From the analysis and the results above we can see that some impurity energy levels in the band gap of GaN (0001) surface are observed, charge transfer occurs from adatoms to GaN (0001) surface. Orbital hybridization at the Fermi level is observed between adatoms and GaN(0001) surface, work function of GaN(0001) surface can be reduced by stronger hybridization. The influence of metal atoms adsorption on the optical properties of GaN(0001) surface is concentrated in the low photon energy region and get weak in the high photon energy region. The red shift of main peaks in the low photon energy region for all the optical parameters is observed, the absorption to visible light and even infrared light is enhanced.

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