Enhancement of ZnO ultraviolet emission by surface plasmon coupling using a rough $NiSi_2$ layer synthesized by ion implantation*

Tan Hairen(谭海仁)[1,†], You Jingbi(游经碧)[1], Zhang Shuguang(张曙光)[1], Gao Hongli(高红丽)[1], Yin Zhigang(尹志岗)[1], Bai Yiming(白一鸣)[1], Zhang Xiulan(张秀兰)[1], Zhang Xingwang(张兴旺)[1], and Qu Sheng(屈盛)[2]

[1]Key Laboratory of Semiconductor Materials Science, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China
[2]Eoplly New Energy Technology Co. Ltd., Haian 226612, China

Abstract: The calculation results of the surface plasmon (SP) energy and Purcell factor of ZnO/$NiSi_2$ demonstrate the possibility of using $NiSi_2$ to enhance the UV emission of ZnO by SP coupling. Experimentally, ZnO films were deposited on $NiSi_2$ layers synthesized by ion implantation, and the roughness of the $NiSi_2$ layers spans a large range from 3 to 38 nm, providing favorable conditions for investigating SP-mediated emission. An 11-fold emission enhancement from the ZnO film on the roughest $NiSi_2$ layer was obtained, which indicates the possibility that metal silicide layers can be used both as an electrical contact and for emission enhancement.

Key words: ZnO film; surface plasmon; $NiSi_2$; photoluminescence
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1. Introduction

Pure metal, such as Au, Ag and Al, has been utilized to enhance the luminescence efficiency of light-emitting materials and devices by means of surface plasmon (SP) coupling of metal with the excited state of emitters, which is called SP-mediated emission enhancement. Giant photoluminescence (PL) enhancement has been demonstrated in several metal/emitter systems; for instance, Ag/GaN[1−3], Ag/ZnO[4, 5], Al/ZnO[6, 7] and Au/CdSe[8, 9]. Recently, Yang *et al.*[10] extended this approach to enhance the electroluminescence of InGaN based light-emitting diodes (LEDs), indicating the importance of SP-mediated emission in improving the efficiency of LEDs. In most LEDs, a metal contact layer for the semiconducting layer in which these excitons are produced usually results in much of the energy being lost to SPs at this interface[11]. If the metal contact layer can be simultaneously utilized to enhance the luminescence efficiency of LEDs by SP coupling, it would be a promising method for developing highly efficient LEDs[11]. In recent years, metal silicides have been applied as contact and interconnect materials for microelectronic devices because of their low electrical resistivity, high chemical resistivity, good thermal stability, and compatibility with modern Si technology[12, 13]. Among the many metal silicides, $NiSi_2$ has been widely studied because of its excellent lattice match with Si[14]. Therefore, the investigation into the feasibility of using metal contact layers such as $NiSi_2$ to enhance the emission of semiconductors by SP coupling will be of great importance.

Wurtzite ZnO is considered to be the most promising material for ultraviolet (UV) LEDs and laser diodes (LDs) because of its large band-gap (3.37 eV) and high exciton binding energy (60 meV) at room temperature (RT)[15, 16]. Therefore, the fabrication of ZnO-based optoelectronic devices has attracted extensive attention recently. However, intrinsic defects in ZnO lead to low UV emission efficiency, which hinders its applications in light emitting devices[15, 16]. More recently, it has been reported that SPs can be used to enhance the band-edge emission of ZnO, however, in previous work, only pure metals (Au, Ag and Al)/ZnO have been utilized to enhance ZnO emission[4−7]. In this paper, the possibility of using a $NiSi_2$ layer to enhance the UV emission of ZnO by SP coupling has been investigated based on calculation of the SP energy and the Purcell factor (F_p) for ZnO/$NiSi_2$. Experimentally, ZnO films were deposited on a $NiSi_2$/Si surface with various levels of roughness, and 2-fold to 11-fold emission enhancements from the ZnO films deposited on $NiSi_2$ were observed, depending on the $NiSi_2$ roughness, which indicates that metal silicide layers can be used both as an electrical contact and for emission enhancement.

2. Experiments

The $NiSi_2$ layers (about 60 nm) on Si (001) substrates ($NiSi_2$/Si) were synthesized by Ni ion implantation into Si wafers using a metal vapor vacuum-arc (MEVVA) ion source operating in pulse mode. The implantation was performed at an extraction voltage of 65 kV to an ion dose of 4×10^{17} cm^{-2} at various mean ion current densities from 6.5 to 26 μA/cm^2. The experimental details can be found elsewhere[14]. The atomic composition of Si to Ni was obtained from Rutherford backscattering spectroscopy (RBS) measurements, and the sto-

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† Corresponding author. Email: hrtan@semi.ac.cn
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ichiometry of nickel silicides (Si/Ni) is close to 2 for all of these samples, thus the obtained materials were denoted as $NiSi_2$. ZnO thin films with a thickness of about 100 nm were deposited on $NiSi_2$/Si and bare Si substrates by RF magnetron sputtering equipped with a ZnO (99.99%) target, as described in Ref. [5]. Typically, the sputtering chamber was evacuated to a base pressure of 1.0×10^{-5} Pa, and then filled with the working gas to a pressure of 1.0 Pa. The ZnO films' growth was carried out in pure Ar ambient at a constant substrate temperature of 400 ℃ and RF power of 80 W. The film thickness was determined by a TENCOR alpha-step profilometer. X-ray diffraction (XRD) measurements were carried out on a Bruker D8 diffractometer. Atomic force microscopy (AFM) measurements were conducted with a Nanoscope IIIa microscope (Digital Instruments) in semi-contact mode. The PL spectra were obtained at room temperature and excited by using a 325 nm He–Cd laser with power of 30 mW.

3. Results and discussion

For SP-mediated emission enhancement, the SP energy of metal must be approximate to the excited energy of the emitters[1−4]. To calculate the SP energy of the ZnO/$NiSi_2$, the dielectric function of $NiSi_2$ should be determined first. In this study, the dielectric function of $NiSi_2$ is calculated by effective dielectric theory, and it can be expressed as[17]

$$\varepsilon_{\text{eff}} = \varepsilon_{\text{d}}\left(1 + \frac{3\phi\beta}{1-\phi\beta}\right), \quad \beta = \frac{\varepsilon_{\text{m}} - \varepsilon_{\text{d}}}{\varepsilon_{\text{m}} + 2\varepsilon_{\text{d}}}, \tag{1}$$

where ε_{eff} is the effective dielectric constant of $NiSi_2$, ϕ is the atomic percentage of Ni in $NiSi_2$, $\phi = 1/3$ is taken as the stoichiometric $NiSi_2$, and ε_{m} and ε_{d} are the dielectric constant of Ni and Si, respectively. The dielectric constant of Ni ε_{m} is described by the Drude model, i.e. $\varepsilon_{\text{m}}(\omega) = 1 - \omega_{\text{p}}^2/\omega^2$, where ω_{p} is the bulk plasmon of the metal, given by $\omega_{\text{p}} = (Ne^2/m\varepsilon_0)^{1/2}$, where N is the number density of mobile charge carriers, e is their charge, m is their mass and ε_0 is the relative permittivity of free space[18]. At the ZnO/$NiSi_2$ interface, the SP dispersion relation can be expressed as[19]

$$\hbar k_{\text{sp}} = \frac{\hbar\omega}{c}\sqrt{\frac{\varepsilon_{\text{eff}}\varepsilon_{\text{ZnO}}}{\varepsilon_{\text{eff}} + \varepsilon_{\text{ZnO}}}}, \tag{2}$$

where k_{sp} is the wave vector of the surface plasmon, ε_{eff} and ε_{ZnO} are the dielectric constants of $NiSi_2$ and ZnO, and $\hbar\omega$ is the SP energy. The calculated dispersion relation of $NiSi_2$/ZnO based on the dielectric functions of $NiSi_2$ and ZnO (Ref. [20]) is shown in Fig. 1(a). As can be seen, the SP resonance energy is about 3.50 eV, which is close to the energy of ZnO band-edge emission (3.27 eV, determined from the PL spectra in Fig. 4). This result shows the feasibility of SP-mediated emission enhancement for ZnO using the $NiSi_2$ layer.

Since the emission enhancement ratio is largely determined by the Purcell factor (F_{p})[21], a simple figure of merit that can be used to quantify the SP-mediated emission enhancement is the radiative recombination ratio (for simplicity, non-radiative recombination was neglected here)[19, 22],

$$F_{\text{p}} = \frac{\Gamma_0(\omega) + \Gamma_{\text{sp}}(\omega)}{\Gamma_0(\omega)}, \tag{3}$$

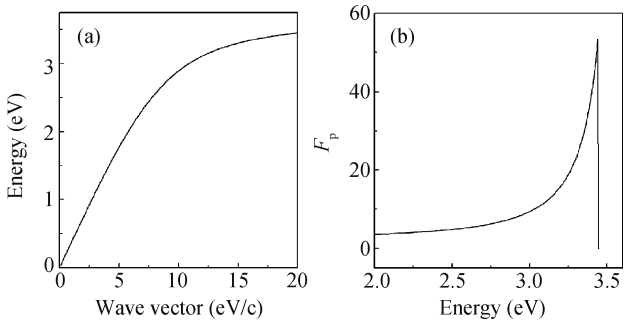

Fig. 1. (a) Surface plasmon dispersion relation of ZnO/$NiSi_2$. (b) Purcell factor (F_{p}) for ZnO/$NiSi_2$.

where Γ_0 and Γ_{sp} are the spontaneous emission rate of the semiconductor and the SP coupling rate, respectively. And Γ_{sp} can be obtained by using the Fermi-golden rule[19, 22] as $\Gamma_{\text{sp}}(\omega) = \frac{2\pi d^2\omega E_0^2(a)}{3\hbar\int_{-\infty}^{\infty}[\partial(\omega\varepsilon)/\partial\omega]E_0^2(z)\text{d}z}\frac{\text{d}(k^2)}{\text{d}(\hbar\omega)}$, where the factor 1/3 comes from the polarization averaging. The spontaneous emission rate can be obtained using the classic formula as $\Gamma_0(\omega) = 4nd^2\omega^3/3\hbar c^3$, where n is the refractive index of the emissive material. Finally, the expression of F_{p} can be given as[19]

$$F_{\text{p}} = 1 + \frac{\pi c^3 E_0(a)^2}{2n\omega^2\int_{-\infty}^{\infty}\partial(\omega\varepsilon)/\partial\omega E_0(z)^2\text{d}z}\frac{\text{d}k^2}{\text{d}\omega}, \tag{4}$$

where E_0 is the unnormalized plasmonic electric field, ε is the dielectric functions of the materials, and a is the location of the emitting dipole relative to the $NiSi_2$/ZnO interface. F_{p} is calculated and the corresponding result is shown in Fig. 1(b). Obviously, F_{p} is strongly dependent on the photo energy and reaches a maximum at 3.5 eV, corresponding to the resonance SP energy of $NiSi_2$. The F_{p} value of ~ 20 can be achieved at 3.27 eV, corresponding to the energy of ZnO band-edge emission, which means that the emission efficiency of the ZnO can be enhanced 20 times with SP coupling when the initial efficiency of ZnO is low[22]. Therefore, it is practicable to enhance the UV emission of ZnO using a $NiSi_2$ layer.

To confirm the calculation results, the PL of ZnO films deposited on $NiSi_2$/Si substrates were investigated. A glancing incidence angle X-ray diffraction (XRD) spectrum of the $NiSi_2$ layer before the deposition of ZnO is shown in Fig. 2. Three diffraction peaks corresponding to the $NiSi_2$ (111), (220) and (311) planes were observed, indicating that polycrystalline $NiSi_2$ was directly formed *in situ* during MEVVA implantation[14]. The XRD pattern of the ZnO film on the $NiSi_2$ layer (measured with a conventional θ–2θ mode) is also shown in Fig. 2. Besides three $NiSi_2$ diffraction peaks, a strong ZnO (002) peak at 34.4° appeared, indicating that the ZnO films were grown along the c-axis orientation on the polycrystalline $NiSi_2$/Si substrates.

For SP-mediated emission, the enhancement ratio is closely related to the surface roughness of metal layers[1, 11]. For metal silicides formed by MEVVA implantation, their surface roughness is strongly dependent on the ion current density due to an extremely high instantaneous beam current density during implantation[23]. Therefore, it is convenient to control the roughness by using different current densities. In this study, four types of $NiSi_2$ layer were fabricated with ion cur-

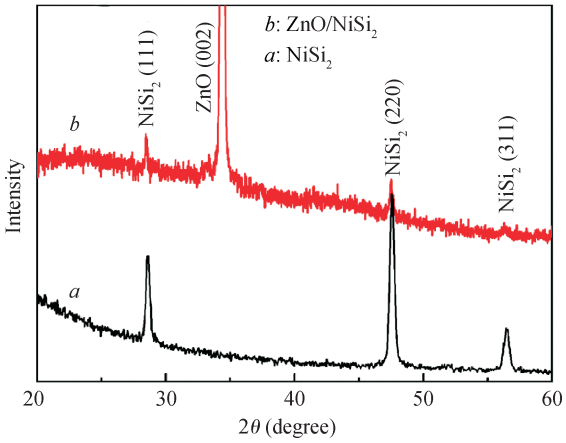

Fig. 2. (*a*) A typical glancing incidence angle XRD spectrum of the as-implanted $NiSi_2$ layer and (*b*) the corresponding θ–2θ XRD spectrum of the ZnO film on $NiSi_2$/Si.

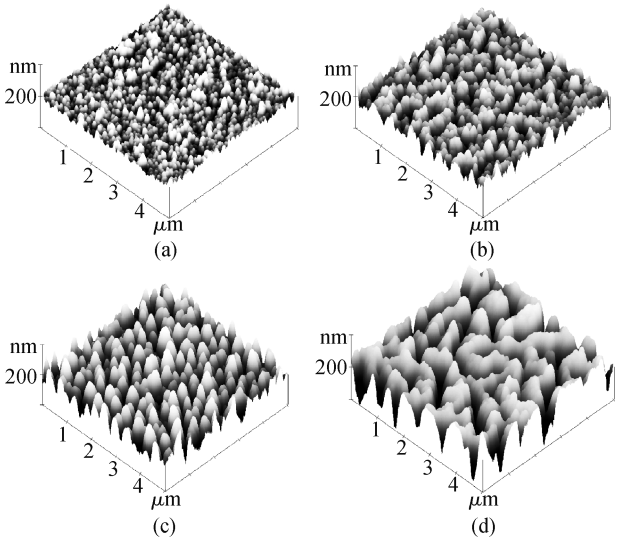

Fig. 3. AFM images of $NiSi_2$ layers implanted with different current densities (a) 6.5, (b) 13, (c) 19.5, and (d) 26 μA/cm^2, and the corresponding R_{rms} is 3, 8, 23 and 38 nm, respectively.

rent densities of 6.5, 13, 19.5 and 26 μA/cm^2. The corresponding atomic force microscopy (AFM) images are shown in Figs. 3(a)–3(d), respectively. The surface morphology of the $NiSi_2$ layers shows similar features of small asperities, but the surface corrugation varies significantly with the current density. Root mean squared roughness R_{rms} is seen to span a large range from 3 nm for the sample with current density of 6.5 μA/cm^2 to 38 nm for the sample with current density of 26 μA/cm^2. A large range of roughness is favorable for investigating the effects of metal surface corrugation on the emission enhancement of semiconductors.

Figure 4 illustrates the room temperature PL spectra of the ZnO films on $NiSi_2$/Si substrates. For comparison, the PL spectrum of the ZnO film directly deposited on Si under the same conditions is also included in Fig. 4 (bottom curve). Obvious band-edge UV emission at 3.27 eV can be found for all of the samples, whereas the defect-related visible emission can be neglected. Importantly, the intensities of UV emission from

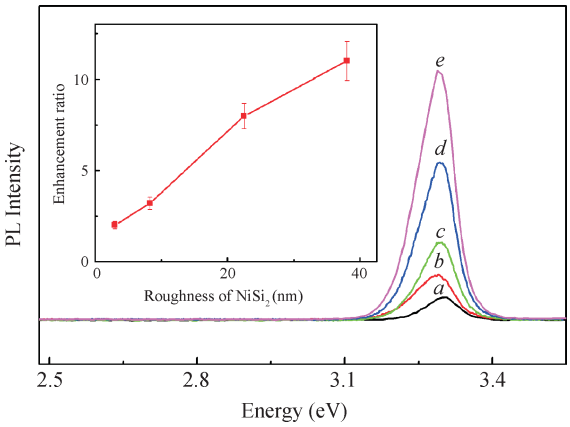

Fig. 4. Room temperature PL spectra of the ZnO films on (*a*) Si, and the $NiSi_2$ layers with an R_{rms} value of (*b*) 3, (*c*) 8, (*d*) 23, and (*e*) 38 nm, respectively. The relationship between emission enhancement ratio and R_{rms} of $NiSi_2$ is shown in the inset.

ZnO/$NiSi_2$/Si are all stronger than that of ZnO/Si. The relationship between the emission enhancement ratio and R_{rms} of $NiSi_2$ is shown in the inset of Fig. 4. It can be seen that the enhancement ratio increases monotonously with increasing R_{rms} of $NiSi_2$. A 2-fold enhancement is obtained for the ZnO film with a relatively smooth $NiSi_2$ surface (R_{rms} = 3 nm), while an 11-fold enhancement is achieved for the ZnO film deposited on a considerably rougher $NiSi_2$ surface (R_{rms} = 38 nm). Obviously, the rougher ZnO/$NiSi_2$ interface is favorable for the emission enhancement, which is consistent with the previous reports on emission enhancement in a pure metal/light emitter system[1, 5, 6]. The energy trapped in the SP modes is dissipated as heat for a smooth metal surface because of the mismatch of momentum between the SP and light, resulting in a small enhancement or even quenching of emission, whereas the rough surface has the ability of scattering SPs, and then these lose their momentum to couple into light. Therefore, emission enhancement can be found when the light-emitting materials placed on the rough enough metal[11]. The dependence of the enhancement ratio on R_{rms} supports the conclusion that SP-mediated emission enhancement exists in the ZnO/$NiSi_2$ system. Additionally, it might be possible that the reflection of the $NiSi_2$ back layer can lead to the enhancement of the ZnO emission to a certain extent. However, the enhancement caused by back reflection is 2-fold at best. Therefore, the 11-fold enhancement cannot be the result of back reflection, and the enhancement of ZnO emission is mainly ascribed to the SP coupling of $NiSi_2$.

Compared with Ag/ZnO or Ag_xAl_{1-x}/ZnO systems[5, 21], the 11-fold enhancement of emission from ZnO/$NiSi_2$ is slightly lower. We suppose that the relatively larger energy gap between the SP energy of $NiSi_2$ and the band-gap of ZnO may be responsible for the smaller emission enhancement. When the excited energy of the emitter deviates from the resonance energy of the SP, a non-resonant coupling process takes place[1]. Since the density of the SP modes is inversely proportional to the slope of the dispersion relation, it reaches a maximum at the resonance energy of SP[11]. Accordingly, for the non-resonance coupling, the density of the SP modes around the emitter will be much lower. Based on the Fermi-golden

rule[19, 22] and Eq. (4), the SP coupling rate Γ_p and the Purcell factor F_p will be smaller, resulting in lower emission enhancement. As can be seen in Fig. 1(b), F_p is about 20 at 3.27 eV for the non-resonance coupling, whereas it is as high as 60 for the resonance coupling. The 11-fold enhancement of emission attained from ZnO on $NiSi_2$ is in reasonable agreement with the calculated F_p. Further study is needed to obtain a giant emission enhancement by tuning the SP energy of $NiSi_2$.

4. Conclusions

The theoretical calculation of the Purcell factor suggests the possibility of using a $NiSi_2$ layer to enhance the UV emission of ZnO by SP coupling. To verify this suggestion, the ZnO films were deposited on a $NiSi_2$/Si surface with various levels of roughnesses. The 2-fold to 11-fold emission enhancement from the ZnO deposited on $NiSi_2$ was observed, depending on the surface roughness of the $NiSi_2$ layers. As metal silicides are frequently used as contact layers, it is possible to use $NiSi_2$ layers as an electrical contact and for emission enhancement simultaneously. Our results indicate that the SP-enhanced emission with $NiSi_2$ is a promising method for developing highly efficient LEDs based on ZnO.

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