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Effect of Pt Interlayer on Low Resistivity Ohmic Contact to p-InP Layer and Its Optimization

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The contact characteristic between p-InP and metal plays an important role in InP-related optoelectronic and microelectronic device applications. We investigate the low-resistance Au/Pt/Ni and Au/Ni ohmic contacts to p-InP based on the solid phase regrowth principle. The lowest specific contact resistivity of Au(100 nm)/Pt(115 nm)/Ni (50 nm) can reach $2.64\times10^{-6}\,\Omega\cdot\mathrm{cm}^2$ after annealing at 380 ℃ for 1 min, while the contact characteristics of Au/Ni deteriorated after annealing from 340 ℃ to 480 ℃ for 1 min. The results of scanning electron microscopy, atomic force microscopy and x-ray photoelectron spectroscopy show that the Pt layer is an important factor in improving the contact characteristics. The Pt layer prevents the diffusion of In and Au, inhibits the formation of Au_3In metal compounds, and prevents the deterioration of the ohmic contact. The metal structures and optimized annealing process is expected to be helpful for obtaining high-performance InP-related devices.

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InP, InGaAs and related materials have been widely applied in both optoelectronic devices and electronic devices, such as photodiodes, laser diodes, and heterojunction bipolar transistors.[1−6] Because of the intrinsic physical properties, InP layers are usually used as the p-cap layers. For example, in the case of InGaAs/InP positive-intrinsic-negative photodetectors, using an InP layer can reduce the dark current and improve the responsivity.[7,8] In the device fabrication process, ohmic contacts with the InP layer are an essential factor. Since the Schottky barrier of p-InP is much higher than that of n-InP, a low ohmic contact to p-InP has been a major concern.[9−11] Various contact schemes have been reported for Au-based low resistance ohmic contacts to p-InP.[12] So far, Au-based metal contacts, such as AuBe, AuZn and other alloy film systems, have been widely used for p-InP layers and met the requirement of low resistance ($10^{-5}\,\Omega\cdot\mathrm{cm}^2$). However, these Au-based metal contacts have poor reliability, rough surface morphology, and deep reaction of the contact materials into the substrates[13−17] and the annealing temperature is relatively high. Therefore, another approach is to use the near-noble metals, such as Ni, Pt, Pd, as the contact metals due to their highly stable properties. In previous studies, contact resistance as low as $10^{-5}\,\Omega\cdot\mathrm{cm}^2$, using Au/Pt/Ni, Au/Pt/Ti and other metal materials, has been achieved. For Au/Pt/Ti, only when the concentration of p-type material surface is greater than $10^{19}\,\mathrm{cm}^{-3}$, it is possible to obtain a contact resistance lower than $6\times10^{-6}\,\Omega\cdot\mathrm{cm}^2$.[18] For an Au/Pt/Ni alloy membrane system, when the p-type material surface concentration is greater than $10^{18}\,\mathrm{cm}^{-3}$, the p-InP contact resistance can be as low as the order of $10^{-6}\,\Omega\cdot\mathrm{cm}^2$.[18,19] At present, reports on the ohmic contact between Au/Pt/Ni and p-InP mainly focus on the specific contact resistance and the change of alloy phase before and after annealing,[19−21] and there are few reports on the ohmic contact optimization of the Pt metal layer.

In this work, we investigate contact characteristics of Au/Ni contact to p-InP, and Au/Pt/Ni contact to p-InP, and obtain the optimized annealing parameters and Pt thickness. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) measurements were performed to characterize the sur-

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face smoothness. X-ray photoelectron spectroscopy (XPS) with sputter depth profiling was performed to explore the stoichiometry and to analyze the formation mechanism of low-resistivity ohmic contact and the contribution of the Pt layer. Moreover, the influence of Pt metal layer thickness on the contact characteristics of Au/Pt/Ni-InP is studied. The optimal Au/Pt/Ni metal structure is expected to provide an experimental basis for preparation and applications of high-performance InP-related micro/optoelectronics.

Experimental Details. We grew the experimental samples on an n-InP (100) substrate by metal-organic chemical vapor deposition (MOCVD), which were used to test the contact resistivity of p-InP. The epitaxial layers consist of a 2.2-μm-thick undoped $In_{0.53}Ga_{0.47}As$ absorption layer (1×10^{15} cm^{-3}), and a 0.6-μm-thick Zn-doped InP window layer ($p\sim 2\times10^{18}$ cm^{-3}). In this experiment, two groups of samples were prepared with Au(200 nm)/Ni(50 nm) and Au(100 nm)/Pt(100 nm)/Ni(50 nm) metal electrodes as p-InP electrodes, which were deposited by Cello Ohmiker-50B electron beam evaporation. Just prior to deposition, the surface of the p-InP window layer was cleaned in trichloroethylene, acetone and ethanol for 5 min sequently, and spray rinsed by deionized water, and blow dried with nitrogen. Then it was etched with a solution of 20% HCl for 1 min, which can remove effectively the native oxide layer on the p-InP.[22] Once the sample was removed from the HCl and blow-dried by nitrogen, it was immediately sent to the electron beam chamber. These samples were then annealed by rapid thermal processing (RTP) in nitrogen ambient at temperature of 340 ℃ to 480 ℃ for 1 min, at intervals of 20 ℃.

The I–V measurement was used to characterize the electrical properties, and the specific contact resistivity was determined using the transmission line model (TLM). According to the TLM, there are seven electrode pads on every specimen with area 200 × 200 μm^2 and space from 10 μm to 40 μm. The surface morphologies of Au/Pt/Ni and Au/Ni after RTP were analyzed by a Hitachi SU5000 SEM as well as an AFM. The Bruker Multi Mode 8 AFM, with a vertical resolution of 0.01 nm and a maximum scanning range of 10 μm × 10 μm. X-ray photoelectron spectroscopy (XPS) with sputter depth profiling was carried out to characterize the metal-semiconductor interactions and stoichiometry. The XPS adopted Thermo Scientific Escalab Xi + microprobe, ion milling for depth profile was performed by an Ar ion beam with 3 kV.

Results and Discussion. Figure 1 shows the I–V curves of Au/Ni and Au/Pt/Ni contacts to p-InP without annealing via TLM measured by Keithley 4200-SCS. Based on the data of Figs. 1(a) and 1(b), it can be determined that the as-deposited contact of Au/Ni is ohmic with specific contact resistance of 4.11×10^{-5} Ω·cm^2 and the value of the contact of Au/Pt/Ni is about 1.6×10^{-5} Ω·cm^2. The only difference between the contact electrodes for both the above structures is that the Au(100 nm) layer in the middle of the metal layer is replaced by the Pt(100 nm) layer, which reduces the contact barrier between the metal and the p-InP before annealing. In order to obtain the optimal ohmic contact to the p-InP layer, rapid annealing treatment is carried out by changing the annealing temperature.

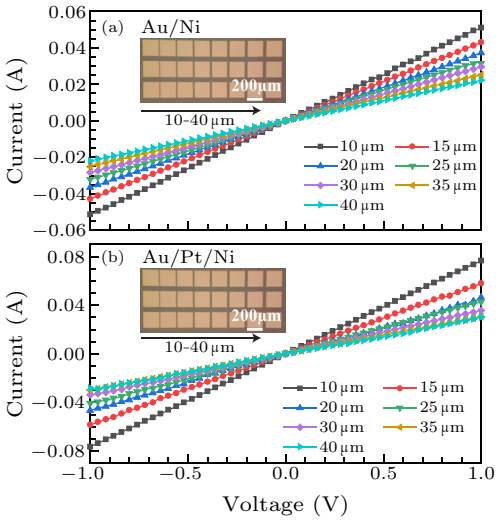

Fig. 1. I–V curves of unannealed (a) Au/Ni and (b) Au/Pt/Ni in contact with p-InP at 10–40 μm TLM spacing. The inserted maps are the microscopic views of the samples under the unannealed condition.

Figure 2 shows the specific contact resistivity as a function of annealing temperature for Au/Ni and Au/Pt/Ni contacts to p-InP, where the annealing time remained unchanged at 1 min. As shown in Fig. 2(a), the minimum specific contact resistance of 5.12×10^{-5} Ω·cm^2 is observed when annealing at 460 ℃ for the as-deposited contact of Au/Ni. However, the minimum specific contact resistance after annealing is also greater than that without annealing, indicating that the contact characteristics of the annealed samples are worse. For the Au/Pt/Ni samples annealed in the temperature range 340–480 ℃ with an increment of 20 ℃, the contact resistivity decreases monotonically to low 7.42×10^{-6} Ω·cm^2 at 380 ℃, and then increases monotonically while the annealing temperature increases from 380 ℃ to 480 ℃, as shown in Fig. 2(b). Strong solid-state reactions are known to occur between the contact metals and the low-melting Group Ⅲ elements and the volatile group-V elements after RTP processing, resulting in complex microstructures and the new alloy compounds.[20] Thus, it can be concluded that the difference of the contact resistance between Au/Ni and Au/Pt/Ni contacts to p-InP is attributed to the Pt interlayer, which results in the different solid-state reactions in the RTP processing.

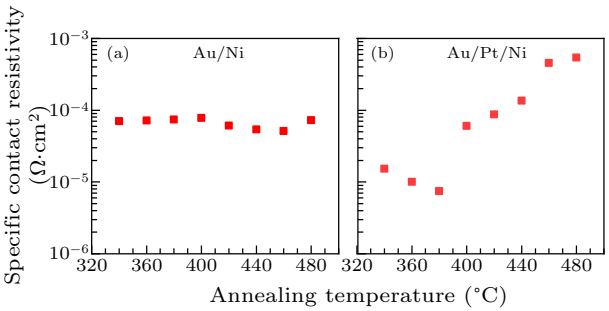

Fig. 2. Contact resistivity as a function of annealing temperature in logarithmic scale for (a) Au(200 nm)/Ni (50 nm) and (b) Au(100 nm)/Pt(100 nm)/Ni(50 nm) contact to p-InP annealed for 1 min.

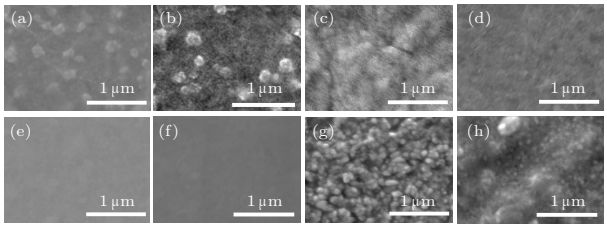

Fig. 3. Surface morphologies of SEM for Au/Ni contacts after RTP: (a) 340 ℃ for 1 min, (b) 380 ℃ for 1 min, (c) 420 ℃ for 1 min, (d) 460 ℃ for 1 min. Surface morphologies of SEM for Au/Pt/Ni contacts after RTP: (e) 340 ℃ for 1 min, (f) 380 ℃ for 1 min, (g) 420 ℃ for 1 min, (h) 460 ℃ for 1 min.

In order to further study the annealing mechanism and to analyze the influence of annealing temperature on contact resistivity, SEM, AFM and XPS measurements were carried out on the annealed samples. Figure 3 shows the surface morphologies of Au/Ni and Au/Pt/Ni contacts with different annealing temperatures studied by SEM. For both contact metal structures, the surface morphologies obviously change with the increase of annealing temperature. When the annealing temperature is 340 ℃ and even much higher, spherical particles form on the surface of Au/Ni alloy, as shown in Figs. 3(a)–3(d), while spherical particles do not form on the surface of Au/Pt/Ni alloy until 420 ℃, as shown in Figs. 3(e)–3(h). This can be explained by the aggregation of the alloying compounds, and Pt acts as an efficient diffusion barrier in the alloying process. Furthermore, Fig. 4 shows the AFM image (5μm × 5μm area) for all the samples and the rms values are all listed in Table 1. For Au/Ni contact metal, the roughness decreases instead of rising as the annealing temperature exceeds 400 ℃, and the contact resistivity is also improved. We analyze that as the annealing temperature increases, the ball polymerizations become larger and gradually agglomerate to form flakes, which can also be inferred from Figs. 3(a)–3(d). For Au/Pt/Ni contact metal, with the annealing temperature decreasing from 460 ℃ to 380 ℃, ball polymerization becomes much milder, the surface roughness decreases and the ohmic contact resistance also decreases, which has been demonstrated in Fig. 2(b).

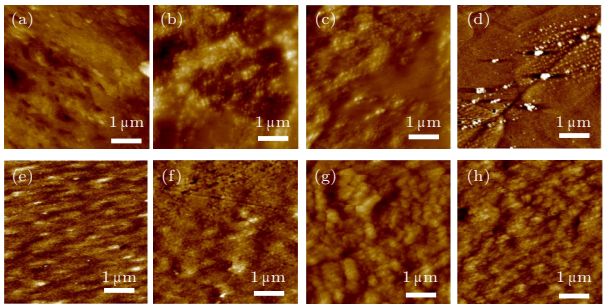

Fig. 4. Surface morphologies of AFM for Au/Ni contacts after RTP: (a) 340 ℃ for 1 min, (b) 380 ℃ for 1 min, (c) 420 ℃ for 1 min, (d) 460 ℃ for 1 min. Surface morphologies of AFM for Au/Pt/Ni contacts after RTP: (e) 340 ℃ for 1 min, (f) 380 ℃ for 1 min, (g) 420 ℃ for 1 min, (h) 460 ℃ for 1 min.

Table 1. Roughness of Au/Ni and Au/Pt/Ni contact interfaces measured by AFM.

Annealed temperature (℃)	Au/Ni (nm)	Au/Pt/Ni (nm)
340	6.74	3.86
380	8.15	3.89
420	6.84	16.0
460	3.06	15.3

To further investigate the effect of the Pt interlayer on the annealing Au/Pt/Ni/p-InP heterostructure, the XPS depth profiles of the Au/Ni and Au/Pt/Ni contact to p-InP were observed after annealing at 340 ℃ for 1 min, which shows the metal-semiconductor interactions and compound distribution. As shown in Fig. 5(a), In has diffused through the Ni layer to the surface of the Au layer, and its content can be up to 80%, while only trace In exists in the Ni layer. In contrast, P is mainly distributed throughout the Ni layer and only a small amount diffuses to the Au layer. This is because Ni and P form stable compounds after annealing at 340 ℃, which prevents further diffusion of P.[22,23] As shown In Fig. 5(a), the content of In on the surface of the electrode is higher than that of Au, and then decreases sharply. It is speculated that the In element tends to diffuse to the surface of the Au layer and gather on the surface during the annealing process.[24] According to previous studies, In and Au diffuse to the surface and will form Au_3In alloy compounds with a very low melting point, and produce small islands, which will increase the specific contact resistance. For the Au/Pt/Ni contact to p-InP, as shown in Fig. 5(b), because the Pt layer prevents Au and In from diffusing to each other during the annealing process, there is no mutual diffusion between In and Au. Therefore, the Au/Pt/Ni ohmic contact changes little after annealing at 340 ℃ for 1 min. In and Au diffuse to a certain extent after the annealing temperature increases to 380 ℃, as shown in Fig. 5(c), indicating that the Pt layer could not well prevent the mutual diffusion of these two elements under this condition. Moreover, Pt diffuses laterally and enters InP through the Ni layer. When the annealing temperature exceeds 380 ℃, In and Au

further diffused into each other while Pt remained basically unchanged. After annealing at 420 ℃, as shown in Fig. 5(d), In diffuses to the surface of the Au layer and the content of In on the electrode surface is higher than that of Au, which increases the surface roughness and reduces the contact resistivity. We consider that when the temperature rises to 380 ℃, the surface of InP layer leaves a large number of In vacancies in the lattice due to the diffusion of In, and Pt will diffuse into the crystal and occupy the In vacancy to become the acceptor impurity, which will reduce the contact barrier, and form low contact resistivity. As the annealing temperature continues to increase, it will intensify the diffusion of In to Au layer and gather on the surface,[24] and Au_3In alloy dominates in the interface layer, which increases the specific contact resistance.[22–25] It can be concluded that the Pt layer is important for improving the ohmic contact, and there is an optimal value for the annealing temperature.

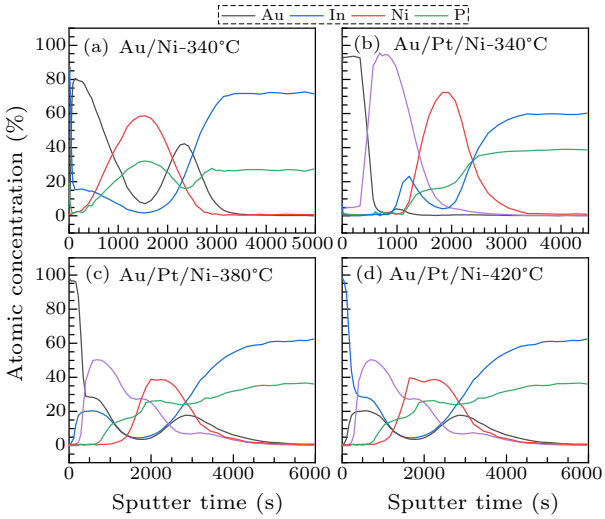

Fig. 5. XPS depth profiles of (a) Au/Ni contact on p-InP annealed at 340 ℃ for 1 min, and Au/Pt/Ni contact on p-InP after annealing at (b) 340 ℃ for 1 min, (c) 380 ℃ for 1 min and (d) 420 ℃ for 1 min.

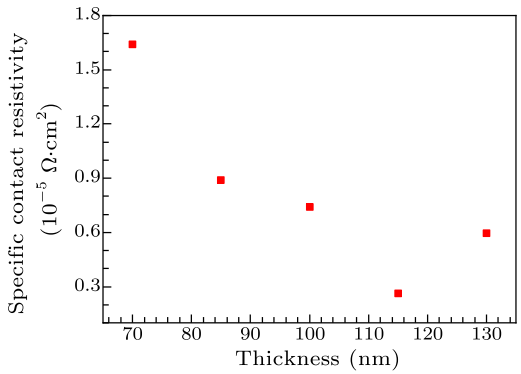

Fig. 6. Contact resistivity as a function of thickness of the Pt layer from 70 nm to 130 nm for Au/Pt/Ni/p-InP after annealing at 380 ℃ for 1 min.

Figure 6 shows the relationship between specific contact resistivity and the Pt layer thickness from 70 nm to 130 nm for Au/Pt/Ni/p-InP annealed at 380 ℃ for 1 min. The optimal specific contact resistivity of 2.64×10^{-6} Ω·cm^2 is obtained when the thickness of the Pt layer fixes at about 115 nm. These results indicate that in the annealing process, the Pt layer needs a certain thickness to effectively block the mutual diffusion between In and Au and to prevent the ohmic contact from getting worse. However, when the thickness of the Pt layer is too thick, it will also lead to increase of the contact barrier and will increase the contact resistivity.

In conclusion, an Au/Pt/Ni ohmic contact to p-InP with a low resistivity of 2.64×10^{-6} Ω·cm^2 has been obtained. The experimental results of SEM, AFM and XPS depth profiles demonstrate that the Pt interlayer is an important factor for improving the ohmic contact, which has an optimal annealing temperature and thickness. Compared to the Au/Ni contact to p-InP, Pt prevents the mutual diffusion of In and Au, inhibits the formation of metal compounds Au_3In with a very low dissolution point, and prevents ohmic contact deterioration in the contact process. This metal structure can be adopted for InP-related materials growth and device fabrication, which could be useful in many kinds of micro/optoelectronic applications.

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