



Preparation of Pt Films on GaAs by 2-step Electroless Plating

Hungsu Im^a, Yong Jun Seo^a, Young Joo Kim^a, Kai Wang^a, Sang Sik Byeon^a,
 Bon Heun Koo^{a*}, Ji Ho Chang^b

^aSchool of Nano Advanced Materials Engineering, Changwon National University,
 Changwon 641-774, Korea

^bMajor of Semiconductor Physics, Korea Maritime University, 1 Dongsam-dong Youngdo-Gu,
 Busan 606-791, Korea

(Received May 14, 2009 ; revised July 17, 2009 ; accepted August 30, 2009)

Abstract

Electroless plating is influenced by kinds of parameters including concentrations of electrolyte, plating time, temperature and so on. In this study, the Pt thin films were prepared on GaAs substrate by a 2-step electroless plating depending method. The small Pt catalytic particles by using Pt I bath exhibited islands-morphology dispersed throughout the substrate surface at 65°C, as function as a sensitized thin film, and then a thicker Pt film grew upon the sensitized layer by the second Pt II bath. As the growth of Pt film is strongly influenced by the plating time and temperature, the plating time of Pt II bath varied from 5 min to 40 min at 60~80°C after Pt I bath at 60~80°C for 5 min. It is found that the film grows with the increasing plating time and temperature. The resistivity value of Pt deposited layer was characterized to study the growth mechanism of 2-step plating.

Keywords: Pt/GaAs, Electroless plating, 2-step plating, FESEM, I-V

1. Introduction

GaAs is a very attractive material for special devices such as high-frequency microwave and optoelectronic devices which perform functions unattainable by Si devices. Performance of GaAs devices is strongly influenced by the electrical properties of metal electrodes and the process of forming these contacts has been developed which provide promising device performance¹⁻³). It is reported that Pt has a high metal work function (6.35 eV) and thermal stability (melting point: 1768°C) to be proper for ohmic contacts of p-GaAs⁴).

Usually, a variety of physical methods such as thermal evaporation, sputtering and electron beam deposition have been used to fabricate metal electrodes for ohmic contacts. However these methods come out weak points during fabricating ohmic contacts, which have complicated vacuum system and heat

damages due to high energy source as well as when plating on metals with 3-dimension shape, which are difficult to get uniform thin film by using these methods. On the other hand, electroless plating method has advantages of low cost, simple equipment, ease of operation, mass production and will expected to makes lower ohmic contact due to its low processing temperature, self-aligning and conformal deposition ability⁵⁻¹⁰).

Electroless plating of metals has significant practical importance in modern technologies, especially in the production of new materials for applications in electronics⁸). There are effects of plating variables including bath concentration, pH, plating time, and temperature etc. Despite its technological importance, the information regarding the electroless plating Pt film is rather limited.

In this study, Pt thin films were prepared on GaAs substrate by a 2-step electroless plating method. The plating time and temperature effects on the performances of Pt films were evaluated.

*Corresponding author. E-mail : bhkoo@changwon.ac.kr

Table 1. Composition of the plating bath

Pt I bath		Pt II bath	
Species	Concentration	Species	Concentration
Na ₂ Pt(OH) ₆	1 g	Na ₂ PtCl ₆	0.562 g
Ethylamine	1 g	NH ₄ OH	10 ml
NaOH	0.5 g	DI water	40 ml
DI water	100 ml	-	-

2. Experimental

The Pt thin films were prepared on GaAs substrate by electroless plating. Prior to the plating, the substrate was first cleaned with acetone, ethanol and distilled water, respectively, and soaked in H₂SO₄:H₂O₂:H₂O=3:1:1 to etch the native oxide layer. The original composition of two kinds of the plating bath is listed in Table 1⁽¹⁾.

2.1 Pt I bath

An aqueous bath containing about 1 g of sodium platinum IV hydroxide, about 1 g of ethylamine and about 0.5 g of NaOH in 100 ml distilled water was prepared. The Pt I bath was conducted on a clean GaAs substrate with additions of proper hydrazine as a reducing agent. The bath was warmed at 60~80°C in steps of 5°C within 5 min.

2.2 Pt II bath

A Pt solution was prepared at a concentration of 0.562 g chloroplatinic acid salt, about 10 ml of ammonium hydroxide and 20 ml of proper hydrazine in 40 ml distilled water. The bath was gradually warmed at 60~80°C with 5 min then the sample was removed from the bath.

The clean GaAs substrate was first plated in Pt I bath, and then plated in Pt II bath, as is called a 2-step plating method. A Field emission scanning electron microscope (FESEM, MIRA II LMH) was used to characterize the surface morphologies of Pt films prepared by each Pt bath, and measure thickness with plating time. I-V characteristics of Pt films after 2-step electroless plating were measured for the contacts between -10 mA to +10 mA in 0.2 mA steps by using a 4 microprobe method.

3. Results and discussion

As shown Fig. 1, FESEM images illustrate the growth morphology of the electroless plating by the Pt I bath on GaAs substrate at different plating

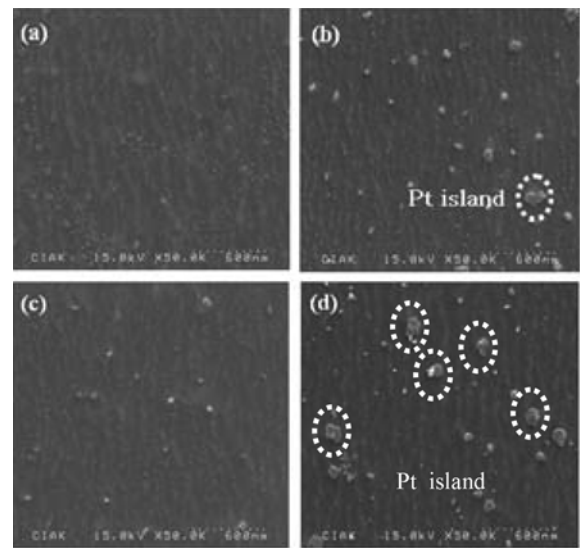


Fig. 1. FESEM images of Pt particles on GaAs by Pt I bath at different plating temperature of: (a) 60°C, (b) 65°C, (c) 75°C, (d) 80°C.

temperature from 60°C to 80°C in steps of 5°C, respectively. It is found that at low temperature of 60°C, no matters were deposited on the surface. After heating up to 65°C, some small Pt catalytic particles exhibited island form dispersed on the GaAs substrate. With the temperature increasing, the number of as-deposited Pt particles increased. These catalytic particles with different sizes sparsely and unevenly dispersed on the sensitized surface of GaAs substrate. The size of these catalytic particles is approximately 60-150 nm. The as-deposited Pt particles were sparsely dispersed^{9,10} but the deposited layer didn't become dense and covered the surface of substrate. Even higher temperature would result in the instability of the electrolytes. It can be concluded that a uniform Pt film can't grow by Pt I bath. Therefore, a sensitized Pt particle dispersed layer (very thin layer less than 10 nm) can be derived by 80°C Pt I bath. It is helpful for the next Pt deposition.

After the sensitized layer on GaAs substrate formed by Pt I bath, the following Pt II bath was applied, in order to grow a thick Pt film on the sensitized Pt layer. Indeed, the first Pt I bath has increased the surface energy, as provided low deposition energy for the growth of Pt by the following deposition. Without exception, the plating temperature of Pt II bath is also a key concerned parameter, which varied from 60°C to 80°C in a step of 10°C. As a result (Table 2), the deposited particles grew and formed continuous thin film and deposits became dense at Pt II bath 80°C, while no films formed and a non-uniform film was observed by

Table 2. Deposition status after using Pt I and Pt II bath with different plating temperature for 5 min

Plating temperature		Deposition status
Pt I	Pt II	
80°C	60°C	No Deposition
	70°C	Deposited
	80°C	Deposited

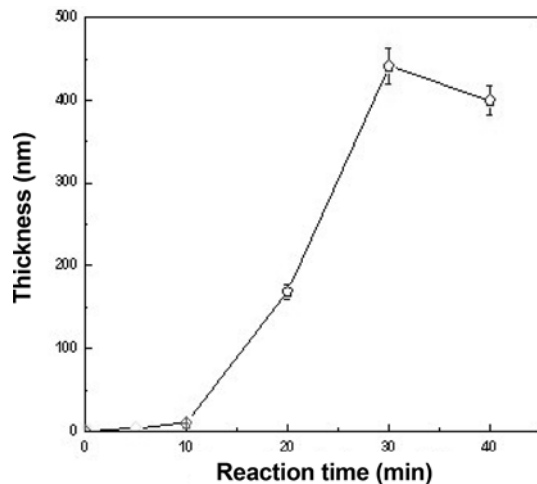


Fig. 2. Thickness by different plating time Pt II bath at 80°C after Pt I bath at 80°C for 5 min.

60°C Pt II bath. Similar to Pt I bath, the plating temperature of 80°C is favorable for the Pt film growth in Pt II bath. And also, even higher temperature would result in the instability of the electrolytes. Therefore, the plating temperature of 80°C is the most feasible temperature for both Pt I and Pt II bath.

Since the deposition of Pt film involves a redox reaction, the growth of Pt film is strongly influenced by the reaction time. To study the plating time effect, Pt II bath were carried out with plating time varied from 5 to 40 min. The total result of thickness calculation was shown in Fig. 2, where it is seen that the thickness obtained in 5, 10, 20, 30 and 40 min is estimated 4, 9, 169, 441 and 400 nm, respectively. In the initial 5 min, no Pt film formed on the GaAs substrate, as plating time is too short. With the plating time increasing from 10 min to 30 min, uniform Pt film formed on the sensitized GaAs substrate by Pt I bath, and the growth Pt film presents a linear trend in the initial 30 min plating time. While the plating is carried out over 30 min, even the thickness became shorter, as means that the reaction rate slows down. It is considered that etching of Pt film happened during long time plating¹²⁾. In all, the proper plating time of Pt II bath

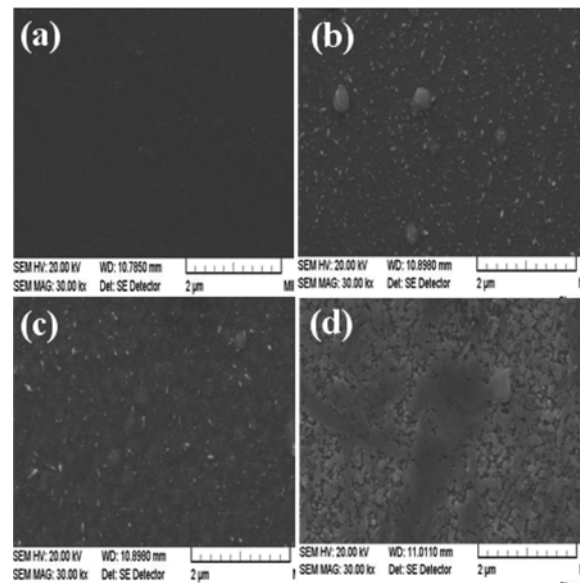


Fig. 3. FESEM surface images of Pt thin film on GaAs by different plating time Pt II bath of: (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min, after Pt I bath at 80°C for 5 min.

is 30 min.

Fig. 3(a)-(d) illustrate the surface morphologies of Pt films obtained by 2-step electroless plating with Pt II bath plating time of 5, 10, 20, 30 and 40 min, respectively. The morphology of 10 min plated sample after 2-step plating looks very smooth with seldom Pt particles distribution. It is believed that a uniform Pt layer grew after 10 min Pt II bath over the sensitized Pt layer after Pt I bath. With further observation, the surfaces of sample (b) and sample (c) are consisted of well combined small Pt particles, which form a uniform Pt layer. More, the surface morphologies of sample (b) and sample (c) are reasonably smoother and denser compared with sample (d). It can be found that the surface morphology of sample (d) became somewhat degraded and pored, where the etching of Pt film happened.

In all, the 2-step electroless Pt plating method can be divided as the generation of sensitized Pt layer and growth of uniform Pt layer. The growth scheme is shown in Fig. 4. In the first step of Pt I bath (Fig. 4(a)), somewhat large catalytic Pt particles sparsely and unevenly dispersed on surface of GaAs substrate, which is ascribed as an island growth mechanism. It can be concluded from the surface SEM morphologies (Fig. 1(d)) that the average size of the large Pt catalyst particles is around 112 nm, and the critical size of the catalyst particles is around 51 nm. The dispersive catalytic Pt particles significantly sensitized the surface, as reduced the deposition

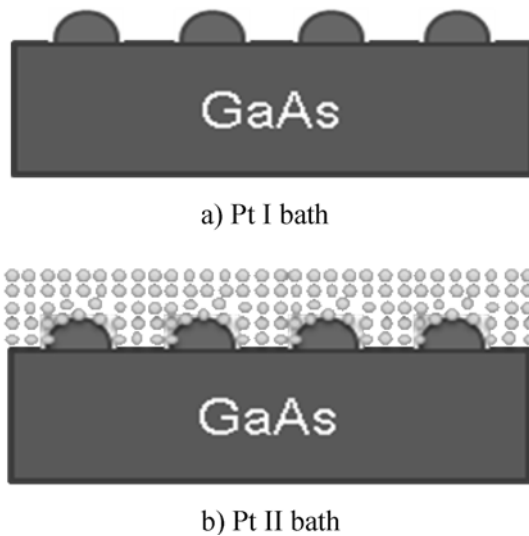


Fig. 4. Film growth schematic of 2-step electroless plating.

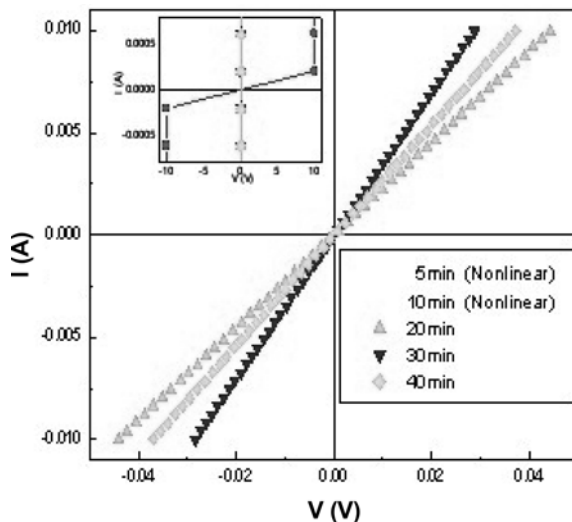


Fig. 5. I-V characteristics of Pt thin film at different plating time of Pt II bath at 80°C after using Pt I bath at 80°C.

energy and set the stage for the further Pt deposition. While in the second step of Pt II bath, tiny Pt particles were reduced and well combined with the substrates, which could repair the surface defects resulted by the previous Pt I bath (as shown in Fig. 4(b)). As a result, a uniform Pt film formed after 2-step electroless plating, which can be observed in Fig. 3(d). With the plating time of Pt II bath increasing over 40 min, the growth of the film finally slowed down and become balanced. Furthermore, this growth mechanism is well proved by the I-V characteristics of Pt films with varied plating time.

With Pt II bath plating time less than 10 min, catalytic Pt particles dominated and dispersed over the GaAs surface. Therefore, there is no doubt that

the I-V characteristic curves of Pt thin films with Pt II bath plating time less than 10 min, presents nonlinear characteristics. When the plating time increased over 10 min, the I-V characteristic curves of Pt thin films surely present linear characteristics. The details with plating time of 20, 30 and 40 min are shown in Fig. 5. The dense and uniform Pt layer contributes to the linear characteristics. The details of measurements show that resistivity is 3.38×10^{-6} , 5.72×10^{-6} and $6.14 \times 10^{-6} \Omega \cdot m$ for the samples plated at 20, 30 and 40 min, respectively.

4. Conclusions

The Pt thin films were prepared on GaAs substrate by a 2-step electroless plating method. The Pt catalytic particles (112 nm in size) by using Pt I bath exhibited islands-morphology dispersed on the substrate over 65°C, as formed a sensitized surface on GaAs. And then by using the second step of Pt II bath, a thick Pt film grew on the sensitized surface. The growth of the Pt films presents an island growth mechanism. Moreover, the film grew with the increasing plating time, and slowed down to balance over 40 min plating.

Acknowledgements

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion KRF-2007-521-D00290). This research was supported by the MKE (The Ministry of Knowledge Economy), Korea, under the ITRC (Information Technology Research Center) support program supervised by the IITA (Institute for Information Technology Advancement) (IITA-2009-C1090-0903-0007).

References

1. M. Murakami, Mater. Sci. Rep., 5 (1990) 273.
2. D. Lamouche, J. R. Martin, P. Clechet, G. Haroutiounian, J. P. Sandino, Solid-state Electro., 29 (1986) 625.
3. H. Chen, C. Hsiung, Y. Chou, Semicond. Sci. Technol., 18 (2003) 620.
4. L. Lewis, D. P. Casey, A. V. Jeyaseelan, J. F. Rohan, P. P. Maaskant, Appl. Phys. Lett., 92 (2008) 062113-1-3.
5. G. Stremmsdoerfer, J. R. Martin, P. Clechet, Nguyen-Du, J. Electrochem. Soc., 137 (1990) 256.

6. C. Flores, *Solar Cell.*, 9 (1983) 169.
7. J. Shu, B. P. A. Grandjean, E. Ghali, S. Kaliaguine, *J. Electrochem. Soc.*, 140 (1993) 3175.
8. R. Chepuri, K. Rao, D. C. Trivedi, *Coordination Chem. Rev.*, 249 (2005) 613.
9. W. L. Liu, W. J. Chen, T. K. Tsai, S. H. Hsieh, S. Y. Chang, *Appl. Surf. Sci.*, 253 (2007) 3843.
10. T. Tsai, C. Chao, *Appl. Surf. Sci.*, 233 (2004) 180.
11. G. O. Mallory, J. B. Hajdu, *Electroless Plating: Fundamentals and Applications*, American Electroplaters and Surface Finishers Society. Chapter 12, William Andrew Publishing/Noyes, Brick, New Jersey (1990) 289.
12. J. H. Kim, S. I. Woo, *Chem. Mater.*, 10 (1998) 3576.