Self-assembly of Pt nanoparticles and their localized surface plasmon-enhanced effects on the optical properties of the polymercrystalline ZnO thin films

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Abstract. In this work, we report that Pt nanoparticles are self-assembled by annealing Pt thin films grown on Si (100) substrates at a high temperature. After growth of Pt thin films, annealing treatment is carried out at 700 and 850 °C respectively, under high purity nitrogen environment. It is found that Pt nanoparticles are formed at annealing temperature of 700 °C, while larger sized and high-quality crystalline Pt nanoparticles are generated at an elevated temperature of 850 °C. It is also found that Pt nanoparticles present plasmon enhanced effect on the optical properties of the polymercrystalline ZnO thin films, and Pt nanoparticles prepared by 20s sputtering time leads to about 5 fold excitation enhancement compared to that without Pt nanoparticles.

1. Introduction
In the past decades, Pt particles have been attracted much attention due to the excellent physical and chemical properties that makes it suitable for the wide application in memory devices [1], sensors [2], catalysis and so on [3, 4]. Garnett et al. demonstrate that Pt particles are favorable to catalysis growth of Si nanowires [5]. One of the most important applications for Pt nanoparticles is employed to promote the property of the sensors [4]. In addition, Pt nanoparticles are used to improve the optical property of the nonpolar ZnO epitaxial layer, showing an about 20 fold enhancement compared to that without Pt nanoparticles [6]. Indeed, polymercrystalline ZnO thin films also have been widely applied in the electrical device and photodevice. Do Pt nanoparticles also significantly enhance the optical property of the polymercrystalline ZnO thin films? This is often neglected.

In this work, Pt nanoparticles are self-assembled on Si (100) substrate by a simply high temperature annealing. And then, the effect of Pt nanoparticles on the optical properties of the polymercrystalline ZnO thin films is also investigated.

2. Experimental
After cleaned by ethanol and deionized water and dried, the Si (100) substrates were transferred into the sputtering instrument chamber. Prior to the growth of Pt thin film, Ar gas was filled into the chamber to avoiding the formation of Pt oxide. 8 mA current was deployed to sputtering the Pt (purity of 99.99%) target to prepare ~7 nm-thick Pt thin films on Si (100) substrates for 100 s at room temperature. And then, as-grown Pt thin films (marked sample A) were annealed at 700 and 850 °C respectively (marked

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as samples B and C respectively) for 2 min using nitrogen (purity of 99.999%) as a protector gas with a heating rate of 2 °C/min. Pt nanoparticles were self-assembled thanks to shrinkage effect caused by high temperature crystallization. The structural and morphological properties of these samples were investigated by X-ray diffraction (XRD, X’Pert Pro MFD) and scanning electron microscopy (SEM, ZEISS Sigma 500).

Similarly, Pt thin films were prepared on the polycrystalline ZnO thin films with a sputtering time of 20, 40, and 60 s, respectively, and followed by the same annealing process at as sample C to fabricating Pt nanoparticles. The optical properties of the polycrystalline ZnO thin films coated Pt nanoparticles was measured by the fluorescence spectrophotometer (FLS, Edinburgh, FLS980).

3. Results and discussion

After preparation, polycrystalline or nanocrystalline Pt thin films are fully covered on the surfaces of Si (100) substrates, as shown in Figure 1(a). Further study shows that there are very small pills on the films (Figure 1(b)). It is widely accepted that high temperature annealing will lead materials to crystallization or recrystallization [5]. As a result, for polycrystalline Pt thin films, nanoparticles are self-assembled due to shrinkage effect caused by crystallization at high temperature annealing, as illustrated in Figures 1(c)-(f). As can be seen in Figure 1(d), 700 °C annealing leads to different size' and dense Pt nanoparticles, and the large size is in the rage of 60-110 nm while the small size is from 10 to 40 nm. When the temperature is increased to 850 °C, the size of the Pt nanoparticles becomes larger, the large ones are enlarged to 80-160 nm, and the number of the small ones is decreased obviously in Figure 1(f). Meanwhile, it should be noted that the edges and corners of the larger Pt nanoparticles are more distinct in Figure 1(f). Compared to 700 °C, 850 °C annealing is more favor for crystallization and produces larger sized nanoparticles (see Figures 1(d) and (f)). Furthermore, shrinkage effect of 850 °C annealing is naturally stronger than that of 700 °C annealing, which accordingly gives rise to larger bareness of substrate surface (Figure 1(b) and (e)).

XRD is employed to further investigate the structure of the nanoparticles. Figure 2 presents XRD patterns of the sputtered films annealed at 700 and 850 °C respectively. Except for Si (400) peak and holder peaks, two very low peaks at 39.507° and 36.122°, corresponding to Pt (111) and (200), can be observed in the sample annealed at 700 °C. On the contrary, obviously, Pt (111) and (200) peaks become strong and sharp for the sample annealed at 850 °C, which indicates high-quality crystalline of Pt nanoparticles. Furthermore, the peak at 32.687° are also observed, which is assigned to Si (200) peak that often disappears. No obvious peaks from Pt oxide can be observed, indicating high purity of the Pt nanoparticles. It is well-known that surface of Si substrate normally owns an ultra-thin SiOx layer owing to natural oxidation. Without etched process, such a SiOx layer helps avoiding PtSi formation by annealing Pt thin film on the Si substrate [5]. As a result, annealing at 700 °C only leads to Pt nanoparticles. Even annealing temperature is further enhanced to 850 °C, metastable Si atoms still will be stopped by the ultra-thin SiOx layer to diffuse into Pt layer and result in PtSi or Pt4Si9 nanoparticles [7]. Thereby, the nanoparticles are only consistent of Pt.
Figure 1. SEM images of Pt thin film (a) and Pt nanoparticles annealed at (c) 700 and (e) 850 °C respectively. (b), (d) and (f) are their corresponding high-resolution images respectively.

Figure 2. XRD patterns of the Pt nanoparticles annealed at 700 and 850 °C respectively.
Figure 3 presents the excitation spectrum of the polymercrystalline ZnO thin films coated with Pt nanoparticles that is sputtered for different times. As shown in Figure 3, Pt nanoparticles play a critical role in the optical properties of the polymercrystalline ZnO thin films. It is noted that the excitation intensity of the polymercrystalline ZnO thin films is sharply decreased with the increase of the sputtering time for fabricating Pt nanoparticles. When the sputtering time is 20 s, the excitation intensity of the polymercrystalline ZnO thin films is about 6 fold of that without Pt nanoparticles. Distinctly, 40 s sputtering time leads to ~35% enhancement in the excitation intensity of the polymercrystalline ZnO thin films when compared with that without Pt nanoparticles. Unfortunately, the excitation intensity of the polymercrystalline ZnO thin films coated with Pt nanoparticles that is sputtered for 60 s, is almost the same as that without Pt nanoparticles. It has been demonstrated that metal nanoparticles own localized surface plasmon enhanced effect for the optical and electrical properties of semiconductor materials, such as GaN [8], ZnO [9], WO$_3$ [10], etc. Similarly, the enhanced excitation of the polymercrystalline ZnO thin films coated with Pt nanoparticles is caused by the plasmon enhanced effect of the Pt nanoparticles. In our work, 20 s of sputtering time is the super one for improving the optical properties of the polymercrystalline ZnO thin film. It is believed that the thickness of Pt thin films is added as the sputtering time increases. Accordingly, the thicker the Pt thin films are, the more area Pt nanoparticles fabricated by high temperature annealing occupies. This means the area for excitation of the polymercrystalline ZnO thin films is reduced with the increase of sputtering time for preparing Pt thin films. As a result, the excitation of the polymercrystalline ZnO thin films is reduced accordingly.

![Excitation spectrum of polymercrystalline ZnO thin films coated with Pt nanoparticles that is sputtered for 0, 20, 40, 60 s, respectively](image)

**Figure 3.** Excitation spectrum of polymercrystalline ZnO thin films coated with Pt nanoparticles that is sputtered for 0, 20, 40, 60 s, respectively

4. **Conclusion**

Pt nanoparticles are self-assembled by high temperature annealing on Pt thin films prepared on Si (100) substrates. SEM and XRD reveal that 700 °C annealing produces Pt nanoparticles, while 850 °C annealing results in larger sized and high-quality crystalline Pt nanoparticles. It is also found that Pt nanoparticles show plasmon enhanced effect in the optical properties of the polymercrystalline ZnO thin films. The excitation of the polymercrystalline ZnO thin films coated with Pt nanoparticles that is sputtered with a time of 20 s, is about 6 fold of that without Pt nanoparticles.

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