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Materials science communication Preparation of platinum silicide films by pulsed laser deposition and pulsed laser annealing

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Abstract

The formation of PtSi ultra-thin films prepared by pulsed laser deposition during pulsed laser annealing has been studied. The growth sequence of the Pt_2Si and the PtSi phases that evolved as the result of the diffusion reaction in the bilayers was examined by X-ray photoelectron spectroscopy (XPS) and the structure characteristics of PtSi were investigated by XPS. X-ray diffraction (XRD) and atomic force microscopy (AFM). Superb uniformity of PtSi films and smooth PtSi/Si interfaces were obtained by pulsed laser annealing. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Pulsed laser deposition; Laser annealing; Nanometer thin film

1. Introduction

PtSi/*p*-Si infrared Schottky barrier detectors (IRSBD) have become one of the most successful photoemissive infrared (IR) detectors [1–5]. Up to now, most of the efforts have been focused on the design of two-dimensional PtSi-SBD arrays for the IR camera. However, little work had been done in the materials science research of PtSi [6,7].

Pulsed laser deposition (PLD) is currently being used to deposit a variety of multicomponent electronic thin films as a materials research tool for the development of next generation electronic devices. In the paper, we prepared the PtSi ultra-thin films by PLD firstly. By studying the kinetics of PtSi formation during various annealing processing, preferred preparing conditions are proposed to form the continuous PtSi ultra-thin film on Si substrate by PLD.

2. Experimental

PLD was used to deposit Pt (a = 0.396 nm) thin films on (100) Si (a = 0.543 nm) substrates that were chemi-

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cally cleaned using a hydrogen passivation technique [8]. A platinum foil (99.999% pure) was used as the target. Irradiations were performed by using a Lambda Physiks LPX 315i KrF excimer laser ($\lambda = 248 \text{ nm}, \tau = 25 \text{ ns}$). A series of pulses were directed to the target surface at a repetition rate of 20 Hz. The laser radiation was focused in order to obtain a typical incident laser fluence of $6 \, \text{J} \, \text{cm}^{-2}$. The laser was incident at an angle of about 45° on the surface of the target on locations slightly eccentric with reference to the geometrical center of the target. In order to obtain irradiation condition as uniform as possible, the target was rotated during the application of the laser treatment with a 5 Hz rotation frequency. All irradiations were conducted inside a stainless steel high vacuum chamber evacuated down to 10^{-7} Pa by a turbomolecular pump. The experimental set-up was designed by the Laboratory of Laser Molecular Beam Epitaxy of Lanzhou Institute of Physics.

Platinum (\approx 10 nm thick) was deposited under a few 10^{-7} Pa, and in situ annealing procedure was carried out continuously using Nd:YAG laser of 1060 nm, 500 μ m pulsed width, and 10 Hz frequency. The laser beam was focused on the rotating disk-like sample within a diameter of 10–20 mm. The base pressure was in the range of 10^{-6} Pa. For comparison, a normal PtSi formation by conventional thermal annealing was also performed. Details are presented elsewhere [9].

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Fig. 1. XPS spectra of Pt4f core line in 3 min laser annealed PtSi/Si sample.

The X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were used for determining the silicide phase and the interface structure. Atomic force microscopy (AFM) was used to observe the surface morphology.

3. Results and discussion

XPS was used to study the formation of PtSi. Fig. 1 shows that the Pt4f spectra of PtSi/Si sample annealed for 3 min and without annealing, respectively. The laser annealing makes Pt doublet shift from lower energy to high binding energy. It indicates that the platinum silicides were formed. According to the normal Pt4f_{7/2} peak position 73.0 eV, the peak value 72.96 eV shows that the single PtSi phase forms, which is also confirmed by XRD pattern as shown in Fig. 2.

After depositing Pt on Si (100) substrates, the thin layer structure of the Pt/Si samples changes sequentially, from Pt–Pt₂Si–Si, Pt–Pt₂Si–PtSi–Si, and Pt₂Si–PtSi–Si to PtSi–Si during pulsed laser annealing for 1–3 min. Fig. 3 shows the Pt4f spectrum of PtSi/Si thin film laser annealed for 1.5 min. The Pt4f_{7/2} signal is observed at 72.5 eV, relative to the normal peak position of Pt₂Si, it is the Pt₂Si peak in the spectrum. That is, Pt₂Si is the first phase to form at the interface between a platinum layer and a silicon layer, and PtSi was formed after all the platinum was consumed to form Pt₂Si. This can be well explained by the dominant diffusing species principle during silicide formation. When



Fig. 2. XRD pattern of PtSi thin films annealing for 3 min.



Fig. 3. XPS spectrum of Pt4f core line of PtSi/Si laser annealed for 1.5 min.

Pt atoms enter the interstitial position of Si lattice and Si atoms got rid of the covalent bond, they mixed together at the interface of Pt/Si during annealing. The composition in the reaction region would be determined by thermodynamic and kinetic conditions during annealing [10–12]. As the forming energy of Pt₂Si phase was 28.8 kJ mol^{-1} and that of PtSi was 33 kJ mol^{-1} [10,13], the mixed atoms on the interface easily formed metastable Pt₂Si, then transformed into PtSi. The velocities of atom diffusion and reaction are controlled by annealing conditions.

Fig. 4 is the profile spectra of 3 min laser annealed PtSi/Si ultra-thin films. It is seen that the interface of PtSi/Si is obvious and smooth and the phase transformation was completed within 1–2 sputtering cycles. There are only two narrow and symmetric Pt4f peaks for any layers, and the layer sequence is likely Pt–Pt₂Si–PtSi–Si in the thin film. During PLD, for the occurrence of melting layer in the Pt/Si heterostructure surface, Pt atoms and Si atoms can diffuse easily in the region of liquid phases. As a result, smooth and sharp interface was formed without the incorporation of other impurity species after the pulsed laser annealing processing.

Fig. 5 shows the surface morphology of PtSi/Si thin films annealed for 3 min by pulsed laser annealing. It can be seen that the surface is continuous and uniform, without any obvious crystalline defects. In addition, we could find



Fig. 4. XPS profile spectra of 3 min laser annealed PtSi/Si samples.



Fig. 5. AFM micrographic of 3 min laser annealed sample surface of PtSi film on (100) oriented silicon substrate.

several grains on the surface of PtSi/Si thin films as the bright projecting part shown in Fig. 4. It has been confirmed that the grains are the monatomic platinum, which were induced during the process of PLD.

4. Conclusions

The high-quality PtSi ultra-thin films with superb uniformity and smooth PtSi/Si interface were formed on Si (100) substrate using PLD following by pulsed laser annealing. It was demonstrated that the formation sequence of PtSi/Si thin films changes from Pt–Pt₂Si–Si, Pt–Pt₂Si–PtSi–Si, and Pt₂Si–PtSi–Si to PtSi–Si with an increase of laser annealing time.

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