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Highly adhesive Pt-electrode films directly deposited on SiO_2 by electron-cyclotron-resonance plasma sputtering

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ABSTRACT

Pt films directly deposited on SiO_2 by electron-cyclotron-resonance (ECR) plasma sputtering and DC-magnetron sputtering have been compared in terms of their performance as electrodes. The DC-magnetron sputtered Pt film consisted of sharply (111) oriented crystallites, which was reflected in hexagonal crystallites observed in atomic force microscopy images. While ECR-sputtered Pt film was also (111) oriented, the X-ray diffraction rocking curve of the (111) peak was broader than that of the DC-magnetron sputtered film. The surface image revealed fine grains, thus having a flatter surface. A scratch test revealed that ECR-sputtered films had an adhesive strength about twice that of DC-magnetron-sputtered films, which was consistent with our tape-test results. Possible reasons for the different adhesion characteristics are discussed.

1. Introduction

Pt thin film has vast fields of application thanks to its excellent properties such as low resistance, chemical non-reactivity, stability at high temperatures, biocompatibility, and smooth surface morphology. Pt-electrode films have been used in biosensors, surface-acoustic wave filters, piezoelectric devices, ferroelectric memories, oxide electronics, and micro-mechanical electro system (MEMS). However, the high melting point of Pt metal does not render convenient thermal evaporation an appropriate route for deposition. The limited processes that are therefore available to deposit Pt films are DC sputtering [1–3], DC-magnetron sputtering [4], RF-magnetron sputtering [5], ion-beam sputtering [6,7], ion-beam-assisted chemical vapor deposition [8], metal-organic chemical vapor deposition [9], molecular beam epitaxy [10], and electron-beam evaporation [11]. Of these, DC-magnetron sputtering is the most widely used because of its high productivity.

Pt films in integrated micro-devices are ordinarily deposited on oxidized silicon wafers. Silica glass substrates are the standard choice for biological and electrochemical applications. However, a problem common to both substrates is their weak adhesive strength when Pt film is directly deposited on SiO_2. Even if a Pt film is stable in its as-deposited state, it may become delaminated when annealed at high temperatures or when an additional layer is deposited on it. Whether or not a particular Pt film withstands the preceding process is hard to predict, since this is determined by complicated parameters including film thickness, temperature, and process gas. To ensure firm contact with the substrate, a Ti or a TiO_2 interlayer, typically 5-nm-thick, is usually inserted [12–14]. The ready nature of Ti to oxygenate and form alloys with other metals renders a Ti or a TiO_2 layer a good candidate to achieve firm contact between SiO_2 and Pt. However, during annealing to crystallize the ferroelectric overlayer film, Ti atoms in the adhesive layer diffuse through the Pt-electrode film into the ferroelectric layer and deteriorate its ferroelectric properties by forming a dielectric layer [15,16]. Furthermore, the absence of a Ti layer is favorable in some applications to achieve better performance. For instance, an adhesion layer should preferably be omitted in cold-cathode electron emitters that are comprised of Pt/SiO_2 or Pt/MgO structures. With respect to Pt and Ag/AgCl electrode pairs employed in biology, a Ti adhesive layer may cause undesirable biological reactions.

In the work reported in this paper, we investigated whether electron-cyclotron-resonance (ECR) plasma sputtering [17] could be used to deposit Pt films without an adhesion interlayer. The ECR sputtering system is comprised of microwave remote plasma generated at low gas pressures with a cylindrical target, which ensures low damage to deposited films. Since the substrate is continuously illuminated with the plasma stream that passes through the center of the cylindrical target, the transfer of plasma energy to the growing film should improve film contact to the substrate. All these features render ECR sputtering similar to ion-beam sputtering or ion-assisted deposition [18–23] while independent ion-beam source is not employed. However, there has not been much work that has investigated the characteristics of ECR sputtering, especially for metal film deposition. Some research has been done on Ta film. Previously, the crystallinity of Ta films deposited by conventional DC

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sputtering and ECR sputtering was closely compared and distinct mechanical properties were clarified [24,25]. The stability of Ta absorbers on SiN or SiC membrane film is an important issue in fabricating the micro-patterns for X-ray lithography masks. The literature has revealed that RF-sputtered Ta films deposited on Si (001) substrates have mainly consisted of a β-phase, which was transformed to an α-phase at sputtering temperatures higher than 270 °C. Ta films ECR-sputtered on Si(001) substrates at 150 °C have an α-phase and are better suited for X-ray mask absorbers since they impose less stress on the mask membrane film.

Motivated by this background, we compared the electrode properties of Pt films deposited by ECR sputtering and conventional DC-magnetron sputtering. Both are mass-production techniques for coating materials. Although many reports have discussed the difference between ion-assisted deposition and unassisted growth (i.e., physical vapor deposition), there has not been much work that has compared different sputtering techniques [26]. Slight differences in film properties can only be highlighted when we have common evaluation tools and conditions. This is particularly the case for the adhesive strength of a series of specimens; they must still be compared under the same measurement conditions with the same film thickness by using the same apparatus. The present scratch test satisfied the above requirements and confirmed the improved adhesive strength of Pt films that were directly deposited on SiO_2 by ECR sputtering.

2. Experimental

Argon was used as a sputtering gas for both the DC-magnetron sputtering and ECR sputtering. Conventional magnetron-sputtering equipment was used in the DC mode at an argon partial pressure of 1 Pa. The ECR sputtering featured a branch-and-connection type ECR source [17]. Here, microwaves transmitted in a waveguide were divided into two equivalent portions and introduced into the plasma source from double silica windows. When the magnetic field was applied, electrons underwent ECR motion, which efficiently excited argons gas to generate dense plasma. Since the windows were not in the line-of-sight of the ECR plasma, the unwanted coating of the windows with sputtered Pt metal was considerably suppressed. When radio frequency power was applied to the target, ions in the plasma struck the inner surface of the cylindrical target and sputtered atoms were deposited on the substrate placed downstream. The operating argon pressure was 2×10^{-2} Pa.

200-nm-thick Pt films were deposited onto a 500-nm-thick SiO_2 layer, which was prepared by thermally oxidizing Si(100) wafers in a hot wall furnace. The as-grown SiO_2 substrates were used without any pretreatment. We denote films deposited at room temperature (RT) as being non-annealed. Deposition by annealing the substrate at 300 °C was also investigated for ECR sputtering. Deposited films was post-annealed in a vacuum at 2.6×10^{-5} Pa. The crystallinity of Pt films was analyzed by X-ray diffraction (XRD) (RINT1500, Rigaku) and the film morphology was evaluated by atomic force microscopy (AFM) (Nanoscope II, Digital Instruments) operated in the tapping mode. The resistivity was measured by using a four-point probe technique.

The method of scratch adhesion testing has been well documented [27,28] and has been applied to TiC [27–29], TiN [30,31], and TiO_2 [32]. The adhesive strength of Pt films to the substrate was examined with a Nano Scratch Tester (CSM Instruments Co.), which is schematically illustrated in Fig. 1. A diamond tip 2 μm in diameter was pushed onto the sample surface and the sample stage was horizontally moved at a rate of 2 mm/min. As the vertical load (F_n) imposed on the sample was linearly increased at a rate of 40 mN/min, the frictional force (F_t) and the vertical position of the tip (d), i.e., its depth of penetration into the film, were continuously recorded. When the critical load was exceeded, the film was destroyed and peeled off. Throughout the scanning procedure for the tip, the trace of the tip engraved into the film was monitored with an optical microscope, which enabled the critical point where the film had been destroyed to be accurately identified. The critical load thus obtained represented the adhesive strength. From three to four measurement scans were attempted for each sample to obtain an average for the adhesive strength.

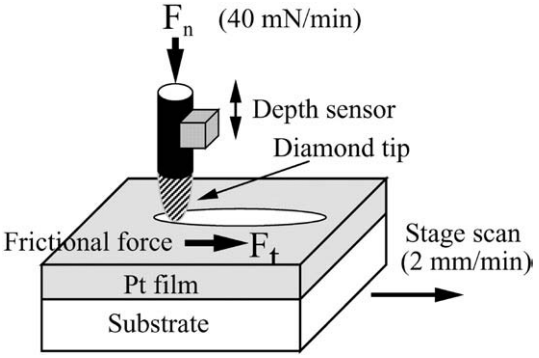

Fig. 1. Underlying principle and measurement conditions for scratch test.

3. Results

All Pt film samples had a mirror-like appearance. Inspecting the surface morphology with an optical microscope revealed a very smooth surface free of three-dimensional microstructures such as hillocks or spikes. Fig. 2 depicts the XRD patterns of an ECR-sputtered Pt film. Intense (111) and (222) peaks with a (311) shoulder appear in the $\omega/2\theta$-scan mode in Fig. 2(a), which indicates that Pt poly-crystals were preferentially (111)-oriented. The 2θ-scan pattern in Fig. 2(b) was obtained at a glancing incidence of X-rays to the substrate surface ($\omega=1.5°$) to maximize sensitivity to the film. Pt (111), (200), (220), and (311) peaks are seen, which means that some misoriented crystallites coexist with those of (111). Fig. 3 depicts similar XRD patterns from the DC-magnetron-sputtered Pt films. Here, the Pt (111) peak in the $\omega/2\theta$-scan mode (Fig. 3(a)) is higher than that in

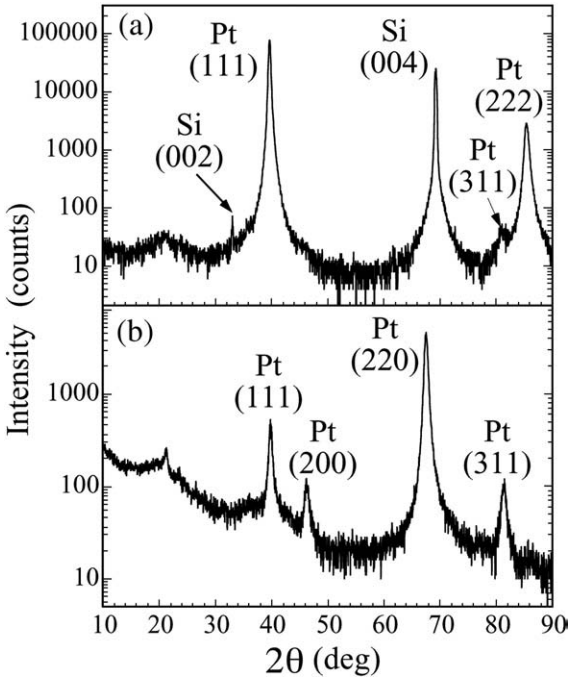

Fig. 2. (a) $\omega/2\theta$-scan and (b) 2θ-scan ($\omega=1.5°$) XRD patterns of Pt films produced by ECR sputtering.