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Electrical and microstructural properties of Ta-C thin films for metal gate

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Abstract

Carbon rich Nano-crystalline grain size tantalum carbide (Ta-C) thin films were prepared by non-reactive simultaneously dual magnetron sputtering. The main purpose of the current work was to investigate the influence of deposition method, deposition power, film thickness and annealing temperature on structural, surface morphology and electrical resistivity of TaC thin films. The experimental result shows that the growth rate of film was about 6.7 nm min⁻¹ and films are growth like spherical structure. The atomic percentage of elements in the films were very sensitive to the deposition power, which even if the small amount of increases in the deposition power of Ta lead the increase of Ta content. However, a small change in Ta percentage did not result in a change in film structure and surface morphology. Annealing temperature did not cause structural changes in the films, but lead small changes in the grain size (range from 7.0 to 9.1 nm) and surface roughness. Resistivity variation of deposited TaC films on the annealing temperature shows random behavior which may cause by the deposition method. Nevertheless, the resistivity of the film decreases first and then increases when the thickness increases from 79.2 nm to 134 nm. Minimum resistivity of film appears at the thickness of 79.2 nm, about 235.2 μΩ.cm. In the end, deposited TaC thin films shows good thermal stability and low enough resistivity for gate electrode application.

1. Introduction

In order to solve the problem of boron penetration [1, 2], gate depletion [3] and fermi level pinning [4] in the metal oxide semiconductor (MOSFET) caused by the reduction of microelectronic device scale, metal gate must be used as the gate electrodes of MOSFET. Among the candidate materials metal carbide is one of the most promising one, because they have excellent properties which satisfy the request for metal gate. Recently, TaCₙ has been studied as a candidate for MOSFET electrode because they have unique properties, such as predominant electrical conductivity (~27 μΩ.cm), thermal stability (Ta₂C and TaC have melting points of 3330 °C and 3985 °C, respectively) [5]. In addition, the reported work function of TaCₙ shows a large variation from 4.18 to 4.8 eV with the difference of Ta/C atomic ratio [6]. These properties can be attributed to the coexistence of metal, ionic and covalent bonds in their structures [7]. Those properties make TaC very attractive for electronic applications [8].

Many studies have been carries out to study the TaC as gate electrodes. Thickness, atomic ratio and heat treatment were the most important parameters to determine the properties of the films. Wan Sik Hwang et al [6] add aluminum in the TaC to increase work function and use it as PMOS (p-type MOSFET) gate electrode. Barinov et al [9] study the influence of heat treatment and metal concentration on the work function and resistivity of TaC. And, Edge et al [10] evaluate the reactive sputtered and non-reactive co-sputtered TaC and compared the influence of deposition various on the work functions and resistivity of the TaC film.

TaC films can be synthesized by various methods such as reactive [8] and non-reactive sputtering [11], chemical vapor deposition [12], atomic layer deposition [13], pulsed laser deposition and ion beam deposition [14]. Among
them, non-reactive magnetron sputtering process is one of the most promising one. Despite many authors have studied non-reactive method to prepare TaC thin film, but most of them were heat the substrate while depositing in order to reach the goal of crystalline of the film [15, 16]. Whereas, in our study we deposit films at room temperature and annealed under high vacuum after deposition was completed. The most considerable advantage of this method was simple process and at low temperature deposition which will not cause the damages of substrate. Furthermore, through this method the percentage of elements in the sample can be specified by changing of the sputtering power. The difference in the proportion of elements will lead to the difference in the sample performance.

In this work, Ta-C thin films were deposited on SiO$_2$/Si by simultaneous non-reactive sputtering of tantalum (Ta) and carbon (C) targets in pure argon gas. Different thickness and different atomic ratio of Ta/C in thin films prepared by changing through the sputtering power and sputtering time applied to targets. After deposition was completed, all samples were annealed at different temperature under high vacuum condition. In the end, the effect of films thickness, atomic ratio and annealing temperature on the films properties have been discussed.

2. Experiment

TaC thin films were prepared by non-reactive simultaneously dual magnetron sputtering on unheated pure Si covered with SiO$_2$ substrate (Which are formed Si/SiO$_2$/TaC structure), using C and Ta targets respectively in pure argon atmosphere (purity of 99.99%) with different thickness and compositions which are controlled by deposition power ratio and deposition time. The carbon target was sputtered with RF (radio frequency) source, while Ta target are sputtered with dc (direct current) source. In order to obtain more uniform thin films layer, rotate the substrate during the deposition was processing. All the shape of the target is pillar with a thickness of 5 mm, a diameter of 60 mm and a purity of 99.99%. Each target was tilted 45° relative to the substrate. The distance between substrate and targets was about 5 cm (If the distance was more than 5 cm, carbon atoms can’t reach to the substrate or the deposition rate of carbon would diminish). The pressure of the reaction chamber was about 1.3 × 10$^{-3}$ Pa before deposition and 0.5 Pa while depositing. The fluent of argon gas during deposition was set by 10 sccm for all the samples. During deposition, no heating or substrate bias were applied on the substrate. Other related parameters were listed in table 1.

After depositions were completed, all samples were annealed under high vacuum (~10$^{-3}$ pa) furnace at 20 min with various temperatures ranging from 400 °C to 800 °C. To avoid the oxidation, all annealed samples were not allowed to remove from the annealing chamber until they had cooled to a sufficiently low temperature.

The crystal structure of the thin film was characterized by grazing incidence x-ray diffraction (GIXRD, D8 ADVANCE, Bruker, Germany) with an incidence angle of 0.8° in order to enhance the diffraction signals of the film compared from the substrate. The surface morphologies, thickness and atomic percentages of elements in the thin films were characterized through scanning electron microscope equipped with energy disperse spectrometry (SEM/EDS, SU8010, Hitachi, Japan). Atomic force microscopy (AFM, Bruker Dimension ICON,

### Table 1. Other parameters of three groups of TaC films and corresponding results.

| Sample | Deposition power (w) | Annealing temperature (°C) | Thickness of films (nm) | Atomic Percentage of (%) (Measured by XPS) | Roughness (nm) | Grain size (nm) (Estimated by S-cherrer formula) |
|--------|---------------------|-----------------------------|-------------------------|------------------------------------------|----------------|----------------------------------------------|
|        | Ta (DC) | C (RF) | Ta | C | O | R$_q$ | R$_p$ |                                |                                     |                               |
| 1-Ta-C | 2  | 300 | 800 | 134 | 5.69 | 79.86 | 14.45 | 7.5 |
| 3  | 300 | 800 | 134 | 10.32 | 64.32 | 25.36 | 9.1 |
| 4  | 300 | 800 | 134 | 10.69 | 62.03 | 27.28 | 3.0 | 2.22 | 7.0 |
| 5  | 300 | 800 | 134 | 11.09 | 61.75 | 27.16 | 5.3 |
| 6  | 300 | 800 | 134 | 12.74 | 54.96 | 32.31 | 7.0 |
| 4  | 300 | 800 | 26.8 | 10.69 | 62.03 | 27.28 | 7.0 |
| 2-Ta-C | 4  | 300 | 800 | 53.6 | 10.69 | 62.03 | 27.28 | 7.0 |
| 4  | 300 | 800 | 80.4 | 10.69 | 62.03 | 27.28 | 2.13 | 1.70 |
| 4  | 300 | 800 | 134 | 10.69 | 62.03 | 27.28 | 3.0 | 2.22 | 7.0 |
| 4  | 300 | As-deposit | 134 | 11.08 | 44.18 | 44.74 | 4.73 | 2.05 | 5.1 |
| 3-Ta-C | 4  | 300 | 400 | 134 | 5.9 |
| 4  | 300 | 500 | 134 | 10.43 | 49.43 | 40.14 | 20.8 | 16.9 | 4.5 |
| 4  | 300 | 600 | 134 | 10.43 | 49.43 | 40.14 | 5.3 |
| 4  | 300 | 700 | 134 | 10.43 | 49.43 | 40.14 | 6.0 |
| 4  | 300 | 800 | 134 | 10.69 | 62.03 | 27.28 | 4.73 | 0.94 | 7.0 |
America) was used to measure the surface morphology and roughness of the film. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher, America) used to characterize the chemical bonding state and chemical percentage of elements in the films. The sheet resistances of the films were measured by Four Point Probe (RTS-8, China).

3. Results and discussions

Figure 1(a) shows the GIXRD patterns of TaC thin films with thickness of 134 nm, atomic ratio of 10.69 at.% Ta, before annealed and annealed at different temperatures from 400 °C to 800 °C. It can be seen that even as before annealing the TaC crystal was already formed and four characteristic peaks can be observed for all cases which are located at 35.2°, 40.9°, 59.2°, 70.8° correspond to (111), (200), (220), (311) crystal plane of TaC phase (JCPDS No. 65-8264). TaC has an NaCl-type face-centered cubic (FCC) structure (Fm3m), with the lattice parameters of $a = b = c = 4.413$ nm and $\alpha = \beta = \gamma = 90^\circ$. And for 700 °C, an additional TaC (222) weak peak appeared at 74.4° compared with others. The (111) main preferential orientation for all the samples is possibly due to the smallest surface energy storage in the stressed state [17]. And from 500 °C to 800 °C intensity of (111) peak become more strengthen and width of peak narrowed which indicate that crystalline of films gets better with the increase of annealing temperature [18]. As you can see from the XRD patterns, with the increase of annealing temperature, positions of related peaks hardly change, this make clear that TaC film has good thermal stability [19]. From those results we can summarize that non-reactive simultaneous sputtering is a good method for obtain a pure and good crystalline of TaC films. The crystal size of film was estimated by Scherer’s formula. Base on this formula, the film’s grain sizes various on the annealing temperatures were listed in table 1. The average grain size of the film ranges from 5.1 nm to 7 nm [15]. It is likely that higher annealing temperature provided energy to atoms to enhance mobility, which can decrease the defects in the TaC films and improve the quality of films [16].

In order to study the effect of Ta content on the crystal structure and grain size of TaC films, the films with different tantalum content were tested by GIXRD. Figure 2(b) shows the GIXRD patterns of TaC thin films with the thickness of 134 nm, annealing temperature of 800 °C and with the different Ta content range from 5.69% to 12.74%. There were four diffraction peaks related to TaC for all the five samples with different atomic ratio. This result is contrary to the view in [10], which holds that TaC crystal can be formed when the content of elements in the film is close to or reaches stoichiometry, otherwise the phase with stoichiometric ratio cannot be formed or only amorphous can be formed. But, in this paper stoichiometric TaC phases was still forms even if the contents of elements in the films were not stoichiometric (the amount of Ta is very small compared with C), which may cause by the different preparation method. However, for the 10.32 at.% Ta and 12.74 at.% Ta, appeared an additional (222) oriented weak peak. And, the difference of atomic ratio did not lead to remarkable change in the position of peaks which indicate that small amount of changes of element contents in the films did not cause...
structural changes of TaC film. The grain size variation of films on the atomic ratio of Ta was displayed in table 1. Related research reports that the size of grains in the film decreases with the increase of C content, which may cause by the excess carbon making grain growth difficult [10]. However, in this work the grain size of films on the atomic percentages of Ta exhibit random behavior which may due to the different deposition method.

XPS was used to characterize the surface atomic percentages, chemical composition and bonding states of the TaC thin films. The variation of atomic percentages of Ta, C and O with the deposition power of Ta listed on table 1. From the table can be seen that with the increase of Ta deposition power, contents of Ta increase (and contents of C decrease) almost linearly. From these result we can deduce that the contents of elements in the deposited films was very sensitive to the deposition power. Figure 2(a) shows the Ta 4f spectra of the films at different atomic ratio of Ta. For all samples, there were three distinct peaks around at 24.0 eV for Ta4f7/2, 26.1 eV for Ta4f5/2, and 28.2 eV for Ta4f7/2 were observed. With the increase of Ta contents, all related peaks shift toward the higher binding energies of 24.1 eV, 26.3 eV and 28.4 eV which close to the typical Ta-C, Ta-O [20], and Ta-Ta [10] binding energy respectively. The appearance of Ta-O bonds may be caused by residual oxygen in the deposition chamber and oxygen contamination of the target material due to contact with air during installation [21], but most probably due to the oxidation of the film surface exposed to air after the deposition and due to the fact that the mono-carbide TaC has a fcc structure where the carbon atoms are located inside the octahedral sites. When the material is nonstoichiometric, the vacant sites can be occupied by oxygen atoms [4]. Further validation will discuss later. Figure 2(b) shows the C1s spectra of films. From the spectra can be observed two peaks located at 283.1 eV and 284.8 eV which are related with Ta-C and C–C. With the increase
of Ta content, Ta-C related peaks become stronger. Meanwhile, intensity of C–C related peaks reduced. These results suggest that the large amount of Ta in the films lead the films to form more C-Ta bonds while the a-C bonds were faded away [8]. Although there are exceed carbon in the films, but there is no obvious peaks appeared from the XRD results related with C phase, possibly due to carbon is amorphous state.

In order to study the effect of annealing temperature on the atomic content, chemical composition and bonding state of TaC thin films, XPS was measured for samples before annealed and annealed different temperatures. According to the XPS results, the content of Ta was decrease slightly with the increase of the annealing temperature probably due to Ta react with residue oxygen in the annealing furnace, the change of percentage in Ta can be seen in table 1. From figure 2(c), it is markedly seen that the feature Ta 4f peak at as-deposition is 23.58 eV (related with Ta-C) and it shifts to the lower energy side with increase of annealing temperature and resolves to 24.1 eV when the annealing temperature reaches to 800 °C. For the other two peaks associated with Ta-O and Ta-Ta, there is no linear relationship between annealing temperature and change in binding energy position. Figure 2(d) displays the C 1s spectra of films. For the films before deposition, there were three peaks associated with Ta-C, C–C and COOR [20]. And with the anneal of film, COOR related peak disappeared (which may lead by unknown reason) and intensity of C–C related peak increase, Ta-C related peak weakened, may be due to the content of Ta decrease with the rises of annealing temperature.

Figure 3 shows the surface scanning and cross-sectional SEM images of TaC films annealed at 800 °C with a thickness of 134 nm and with different atomic percentages of Ta range from 5.69% to 12.74%. From the images of from (a) to (c), it can be seen that the film grows very evenly and shape of the grains was like spherical. The change of grain size in the film is very small with the change of atomic ratio. From the cross-sectional SEM images of TaC film, shows in figure 3(d), can be seen that the films layer was clearly separated from the substrate which indicate that there was not take place diffusion between film layer and substrate, which indicate that TaC films shows its high temperature stability. Furthermore, the film possesses a uniform thickness of approximately 134 nm (deposition time was set by 20 min), and so the deposition rate of films based from it was approximately 6.7 nm min⁻¹.

Figure 4 shows the full elements XPS spectra and energy spectrum (EDS) of TaC thin films with thickness of 134 nm, annealing temperature of 800 °C and deposition power of Ta and C were 5 w and 300 w respectively.
And table 2 display a comparison of atomic percentages of elements in TaC thin films measured by XPS and EDS, respectively. As can be seen from table 2, the atomic percentage of element in the film measured by XPS and EDS is quite different, especially the atomic percentages of oxygen, the amount of oxygen in XPS data is much larger than that in EDS data. In addition, the substrate content is zero in XPS measurement, while the Si content is very large in EDS measurement. Those difference probably lead by the different working principles of these two method. In addition, for XPS detection, the signal originates from a depth of several nanometers from the sample surface, while the EDS signal originates from a depth of several hundred microns from the sample surface, i.e. Therefore, XPS can reflect the percentage of elements on the sample surface, while EDS detects the percentage of atoms in the whole particle within a certain range. From this point of view, XPS measurement is much more reliable than EDS measurement in order to predict the atomic percentage of elements [22]. Therefore, in this paper we determine the atomic contents of Ta by XPS measurement. From the above experimental results can be roughly predicted that oxygen pollution on the film surface is more serious than that in the whole film volume. However, there are no oxygen-related diffraction peaks in the XRD spectrum of the thin film, as shown in figures 1(a) and (b), while in the XPS data can be observe strong Ta-O related peaks, probably due to the fact that TaOx phase is amorphous.

In order to study the influence of films thickness and annealing temperature on surface morphology and roughness, AFM was measured, showed in figure 5. The films were composed of column-liked crystals. The surface roughness of the film was increased with the thickening of the films. And, as the increase of annealing temperature the particles were coalesce, and surface roughness increase firstly then reduce that may one of the factor which may lead to randomness of resistivity with annealing temperature, as shown in figure 6(b).

Figure 6(a) shows the resistivity dependence on thickness of TaC film, with Ta atomic percentage of 10.69%, after annealing at 800 °C. The relationship between resistivity and thickness can be divided into two steps. Firstly, resistivity was decreased with the increase of film thickness, and then was a small increasing trend from 79.2 nm to 132.4 nm. The resistivity at 79.1 nm thickness is the smallest, about 235.2 μΩ.cm. This patterns of changes of films resistivity was agreed with [23]. According to the Matthiessen’s rule [24], film resistivity can be written as

\[ \rho = \rho_b + \rho_i + \rho_g + \rho_s \]

Where \( \rho_b \) is the bulk resistivity determined by composition and phase, and \( \rho_i, \rho_g, \rho_s \) are the resistivity related to impurities, grain boundary and surface scattering. Because of other deposition parameters was being fixed in this
work, but films prepared with only variation in deposition time which cause the variation of film thickness, hence the resistivity of films were mainly depend on the grain boundary ($\rho_g$) and surface scattering ($\rho_s$).

As aforementioned, the evolution of resistivity can be divided into two stages. At the first stage, with the increase of film thickness, small grains aggregate, and this aggregation was leading to the decrease of grain boundary scattering, therefore, the resistivity $\rho_g$ related to grain boundary scattering is reduced. However, in the second stages, thickness larger than 79.2 nm, although the amount of small grains still increases, but the roughness of surface was increased, shows in figures 5(a) and (b), which lead to increase of the resistivity $\rho_s$ related to surface scattering, and this become the main factor to influence the total resistivity.

Figure 6(b) shows relationship between resistivity and annealing temperature of TaC thin film. Although many researchers have proved that the resistivity of the film decreases with the increase of the annealing temperature, this is due to the improvement of the crystallinity of the film and the reduction of defects in the film, which in favor to electrical conductivity, as the annealing temperature [25]. However, in this paper the
variation of resistivity of TaC thin films on annealing temperature shows random behavior. This randomness may be due to the different preparation processes and the above-mentioned factors which influence films resistivity combined affect. Nevertheless, except for the high resistivity of films annealed at 700 °C (resistivity of 1332 μΩ.cm, may be caused by the arise of extra (222) oriented peak), the resistivity of other samples are not very big (316 ~ 917 μΩ.cm). In a word, deposited TaC thin films show low enough resistivity for gate electrode application which should be less than about 1000 μΩ.cm [26].

In conclusion, carbon rich Nano-crystalline size tantalum carbide (Ta-C) thin films were prepared by non-reactive simultaneously magnetron sputtering. The experiment result shows that percentage of Ta was increase with the rises of Ta deposition power. However, the slight change of Ta content does not lead the changes of crystal structure and surface morphology of the thin film. And annealing temperature did not cause any phase transform in the films which reveal good thermal stability of films. The growth rate of the film is 6.67 nm min⁻¹. Resistivity of film decreases firstly with the increase of films thickness, then has a little increasing trends when the thickness rise from 79.2 nm to 134 nm. And then, the changes in resistivity of films on the annealing temperatures express random behaviors, may be due to the different deposition method. In short, the TaC thin film prepared in this paper has good thermal stability and low resistivity, which meets the application requirements of metal gates.

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