Extended Abstracts of the 20th (1988 International) Conference on Solid State Devices and Materials, Tokyo, 1988, pp. 89-92

Evaluation of Laser CVD Tungsten for Gate Electrode

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The properties of tungsten (W) films deposited by ArF excimer laser CVD using WF_6 and H_2 gases, and the chracteristics of MOS capacitors with laser CVD-W gates were studied. The intrinsic stress of W films varies from large tensile to small compressive with increasing H_2/WF_6 gas flow ratio. It has been found that W films are reproducibly deposited on SiO_2 without peeling off when the intrinsic stress of W is less than 4×10^9dyne/cm^2 (tensile). MOS capacitors were fabricated by depositing these films and their characteristics were compared with those of sputtered-W gate capacitors. The contamination due to mobile ions is extremely lower than that of sputtered-W gate capacitors.

1. Introduction

Tungsten is an attractive alternative of poly-Si or polycide for VLSI CMOS gate electrodes because of its low resistivity and near midgap work function[1]. W gates are commonly prepared by sputtering, electron beam evaporation[2], or chemical vapor deposition (CVD)[3][4]. The CVD method has several advantages in comparison with the others, that is, excellent step coverage over SiO_2 steps, low contamination and low resistivity. In addition, the CVD method gives no damage to gate oxide during deposition. However it is impossible to apply the usual thermal CVD using WF_6 and H_2 gases to the fabrication of W gates because, in this method, W films are only selectively deposited on Si but not on SiO_2 around 400°C. To solve this problem, various non-selective CVD methods[3][4] were investigated. However, W films deposited by non-selective CVD usually exhibit uncontrollable large intrinsic tensile stress about 1×10^{10}dyne /cm^2, which is a cause of frequently observed peeling of W films from SiO_2 and may induce damage to gate oxide.

We adopted the ArF excimer laser CVD using WF_6 and H_2 gases as non-selective CVD method and investigated properties, particularly stress, of W films as a function of deposition parameters. It is shown that the intrinsic stress of W films can be controlled by selecting the deposition parameters. Using W films having low intrinsic stress, laser CVD-W gate MOS capacitors were fabricated and their characteristics were compared with those of sputtered-W gates.

2. Experimental

W films were deposited on Si or SiO_2 at 400°C using WF_6, H_2 and Ar gases by ArF excimer laser CVD. The ArF excimer laser was oparated at 50 Hz, 150 mJ/pulse, and the laser beam (20 x 8 mm) was passed 10mm above the substrate. W films deposited on SiO_2 were annealed in a furnace of N_2 atmosphere at temperature higher than 800°C to improve the adhesion between W film and SiO_2. W-gate MOS capacitors were fabricated by depositing 300nm thick W on SiO_2 grown on p-type (100) 3Ωcm Si substrates. Mobile ions in gate oxide were measured by triangular voltage sweep (TVS)[5] and SIMS.

3. Results and Discussion

3-1. Film Properties and Adhesion

The stress of W films as a function of the H_2/WF_6 gas flow ratio (k) is shown in Fig.1. The stress of W films was calculated from curvature of 4 inch Si wafers on which 300nm thick W films were deposited. When the WF_6 flow velocity (S_{WF6}), which is defined as the ratio of WF_6 flow rate to the total pressure, is 0.08sccm/Pa, the film stress is large regardless of k. On the other hand, at S_{WF6}=0.01sccm/Pa, the stress changes from large tensile to small compressive with increasing k. This decrease of the film stress occurs under the condition that the deposition rate of W depends on the WF_6 flow velocity, that is, the supply of WF_6 is insufficient. In this case, We can control the film stress reproducibly.

When the tensile stress of W films were more than $4X10^9$dyne/cm^2, W films were peeled off from SiO_2 during the deposition or subsequent annealing process. On the other hand, when the stress was compressive, small bubbles were observed at W/SiO_2 interface. In order to deposit W films on SiO_2 without peeling off, the stress must be controlled in the range from nearly zero to tensile stress less than $4X10^9$dyne/cm^2.

However these W films did not always satisfy the adhesive tape test (using a kokuyo T-H12 tape). To improve the adhesion, we adopted a high temperature annealing. Shintani et al.[3] have recently reported that film adhesion is improved by annealing. In our experiment, the adhesion between W film and SiO_2 was improved by the annealing at higher temperature than 800℃ for 30min in N_2 atmosphere and all films satisfied the adhesive tape test.

Fig.2 shows the resistivity of W films as a function of k before and after annealing at 1000℃ for 30min. The resistivity of films before annealing was 12~15 $\mu\Omega$·cm regardless of k. Nikou[6] reported that W films deposited by sputtering with low stress about 1.5~2.0X10^{9}dyne/cm^2 have β-W structure and higher resistivity than 100$\mu\Omega$·cm. In our case, all W films deposited under any conditions have α-W structure. On annealing at 1000℃, the resistivty of films were reduced to about 10$\mu\Omega$·cm, which is lower than that of sputtered-W.

Fig.3 shows the variation of stress with the annealing temperature for laser CVD-W and sputtered-W. All data were obtained from stress measurement at room temperature after annealing for 30min. The stress of

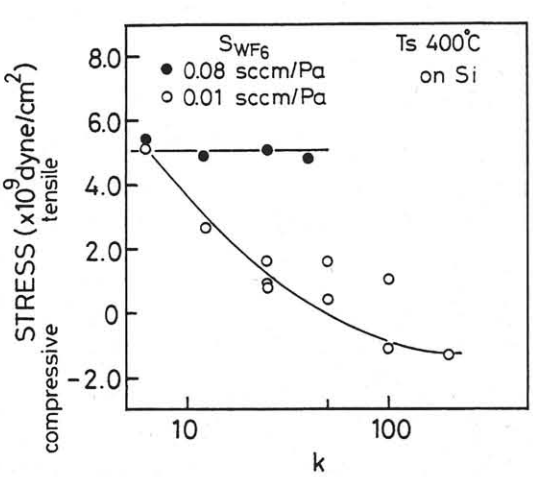


Fig.1 Dependence of laser CVD-W stress on the H_2/WF_6 gas flow ratio (k).

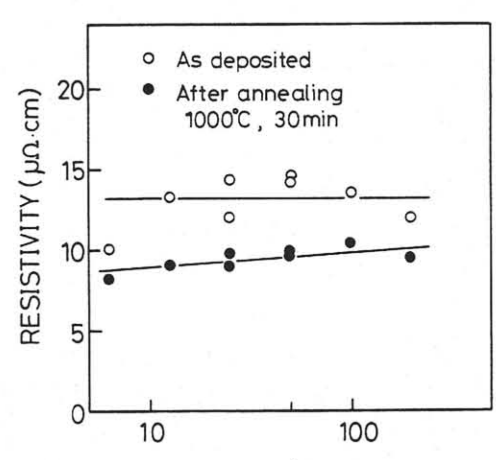


Fig.2 Dependence of laser CVD-W film resistivity on the H_2/WF_6 gas flow ratio (k) before and after annealing.

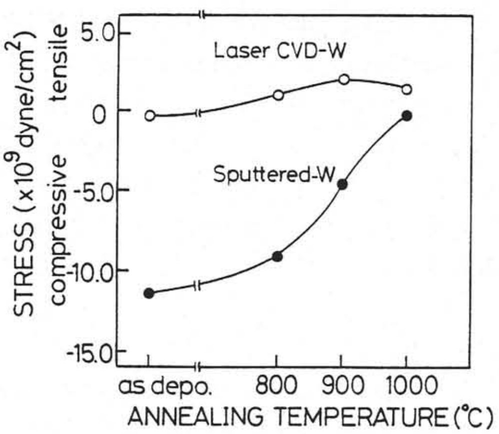


Fig.3 Variation of stress with annealing temperature for laser CVD-W and sputtered-W.

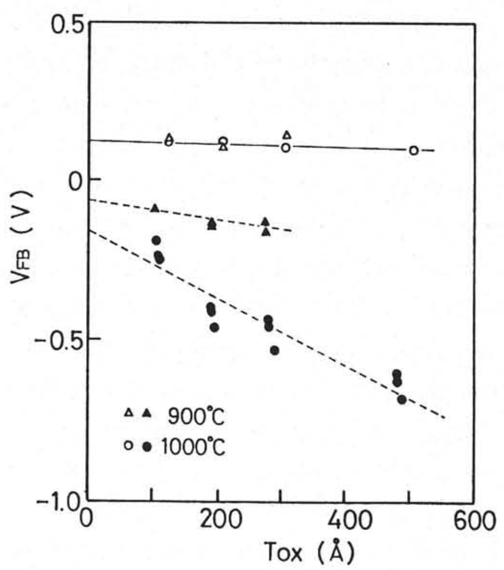


Fig.4 Flatband voltage (V_{FB}) as a function of gate oxide thickness (T_{OX}) after annealing. Laser CVD-W:○ △ ;Sputtered-W:● ▲

laser CVD-W as deposited is about $5X10^8$dyne/cm^2 (compressive), which was controlled by selecting deposition parameters as mentioned before. The stress increases gradually with increasing annealing temperature, but the maximum stress of laser CVD-W is small (about $2X10^9$dyne/cm^2). This value is nearly equal to the thermal residual stress of W[7]. On the other hand, the sputtered-W has high compressive stress as deposited and the stress decreased rapidly with increasing annealing temperature.

3-2. MOS Characteristics

Fig.4 shows the flatband voltage (V_{FB}) obtained by C-V measurement as a function of the gate oxide thickness (t_{OX}) for MOS capacitors with laser CVD-W and sputtered-W gates after high temperature annealing. For laser CVD-W gate, the slopes of the curves are small and nearly independent of annealing temperature. In contrast to that, for sputtered-W gates, the slope rapidly increases with annealing temperature. The fixed charge density (Q_f) was caluculated from these slopes. The Q_f value of laser CVD-W gates is $1.60X10^{10}/cm^2$, which is nearly equal to that of poly-Si gate. The Q_f value of sputtered-W gates is much higher than that of laser CVD-W gates. The values, $6.12X10^{10}/cm^2$ and $2.22X10^{11}/cm^2$, were obtained for samples annealed at 900 and 1000℃, respectively. These results indicate that MOS capacitors with laser CVD-W is stable for high temperature annealing.

The characteristics of the MOS capacitor with laser CVD-W gate is shown in Table.1 as compared with those with sputtered-W gates (I), (II) which were prepared using two different targets whose purity are 99.995%. These samples were annealed at 900℃ for 30min. The flatband voltage and the maximum breakdown field of the capacitor with laser CVD-W gate are almost the same as those with sputtered-W gates. However, it is

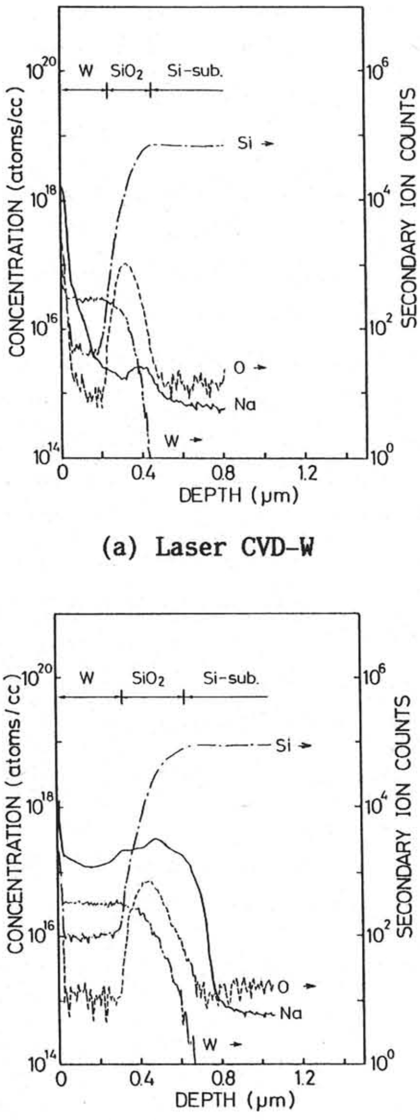
Table.1 Comparison of W gate MOS characteristics. Thickness of gate oxide: 10-13 nm ; Annealing temperature: 900℃

	Laser CVD-W	Sputtered-W (I)	Sputtered-W (II)
V_{FB} [V]	0.1	0.0	-0.1
Em [MV/cm]	11	11	11
D_{ion} [cm^{-2}]	$<5\times10^9$	3×10^{12}	7×10^{10}

V_{FB} : FLATBAND VOLTAGE
Em : MAXIMUM BREAKDOWN FIELD
D_{ion} : MOBILE ION DENSITY MEASURED BY TVS METHOD

noticeable that the mobile ion density of the capacitor with laser CVD-W gate is below the detection limit of the TVS method. The mobile ion density of the capacitor with sputtered-W (II) is much less than that with sputtered-W (I), but it is still detectable.

Na depth profiles were analyzed by SIMS in both laser CVD-W gate and sputtered-W gate (I) capacitors, and shown in Fig.5. The Na concentration in the sputtered-W (I) is very high, and the SiO_2 layer is also contaminated with Na at the same level as that in W. But the Na concentration in laser CVD-W is suppressed remarkably under low level except for the surface region, which may be contaminated during fabrication process, and the level of the contamination in SiO_2 is also extremely low. These facts indicate that the contamination in laser CVD-W is extremely lower than that in sputtered-W.



(a) Laser CVD-W

(b) Sputtered-W (I)

Fig.5 Comparison of Na profiles analyzed by SIMS in MOS capacitors.

4. Conclusion

W films with nearly zero intrinsic stress are reproducibly deposited by ArF laser CVD. Using these films, MOS capacitors were fabricated. The characteristics of these laser CVD-W gate capacitors are stable for high temperature process up to 1000°C. In addition, the contamination due to mobile ions is extremely lower than that of sputtered-W gate capacitors. These results indicate that laser CVD-W is a promising material for the gate electrode of VLSI.

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