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In situ barrier formation using rapid thermal annealing of a tungsten nitride/polycrystalline silicon structure

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This letter describes the use of rapid thermal annealing (RTA) to form a barrier layer applicable to the gate electrode in dynamic random access memory devices with a stacked structure [tungsten nitride (WN_x)/polycrystalline Si (poly-Si)]. After RTA, the reactively sputtered amorphous WN_x film on the poly-Si was transformed to a low-resistive α-phase W and nitrogen-segregated layer. Most of the nitrogen in the WN_x film was dissipated and a relatively small amount of the nitrogen was segregated at the interface of the α-phase W and poly-Si. The segregated layer was estimated to be 2 nm thick and revealed a silicon nitride (Si–N) bonding status. More importantly, we found that this thin segregated layer successfully protected the formation of tungsten silicide, even after RTA at 1000 °C for 2 min in a hydrogen environment. © *2000 American Institute of Physics.* [S0003-6951(00)03418-5]

As ultra-large-scale integrated circuit devices are scaled down to a deep submicron regime, the gate resistance/capacitance time delay limits the speed of metal–oxide–semiconductor devices. To reduce this delay, a gate structure with a low-resistive material has been widely investigated.[1–3] A stacked gate structure, tungsten (W)/barrier/polycrystalline Si (poly-Si), is considered to be a promising candidate to replace the tungsten silicide (WSi_x) or a self-aligned silicide (salicide) gate, due to its low electrical resistance and high resistance against agglomeration during annealing.[4,5] For example, the sheet resistance of the gate structure of W(100 nm)/WN_x(5 nm)/poly-Si(100 nm) was estimated to be 1.5 Ω/sq, which is lower by one order of magnitude compared with that of the conventional gate structure of WSi_x(100 nm)/poly-Si(100 nm). Moreover, this low sheet resistance was able to reserve even at a narrow gate linewidth of 0.12 μm.[6]

Because direct contact of W to poly-Si results in the formation of WSi_x during annealing at temperatures above 600 °C, a barrier layer such as titanium nitride (TiN) and tungsten nitride (WN_x) jams in between them.[7–9] The W film in the W/WN_x/poly-Si structure revealed a lower sheet resistivity than that in the W/TiN/poly-Si structure.[6] In addition, better oxide integrity at the edge of the W/WN_x/poly-Si gate was shown compared with the W/TiN/poly-Si structure after selective Si oxidation that was conducted for etch damage recovery.[10] However, WN_x is known to be unstable and easily transform to W and nitrogen at temperatures above 800 °C, resulting in the formation of WSi_x at the interface of W/WN_x and poly-Si during the next high-temperature process, such as selective Si oxidation and dopant activation.[11] Therefore, a highly reliable diffusion barrier layer is essential between W and poly-Si.

In this study, we propose a method of forming a barrier layer for the W/poly-Si gate structure with a WN_x film on poly-Si by rapid thermal annealing (RTA). To make the sample structure, the WN_x film (100 nm) was reactively sputtered on a doped poly-Si film that had been cleaned by HF. Then, RTA was performed at temperatures ranging from 600 to 1000 °C under nitrogen atmosphere for 1 min. Rutherford backscattering spectroscopy was employed to quantify the composition of the WN_x film, and secondary ion mass spectroscopy (SIMS) was used for compositional analysis. Electrical resistivity was evaluated using a four-point-probe method was phase identification was carried out using Θ–2Θ x-ray diffraction with a scan rate of 0.2°/min. Also, the microstructure and chemical status at the interface of W and poly-Si were analyzed by transmission electron microscopy (TEM) and x-ray photoelectron spectroscopy (XPS).

Figure 1 shows the variation of the resistivity and the

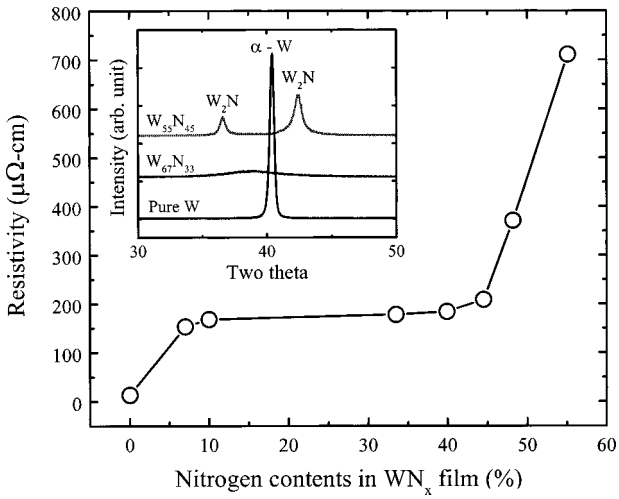

FIG. 1. Resistivity and x-ray diffraction spectra of WN_x as a function of nitrogen content in as-deposited film.

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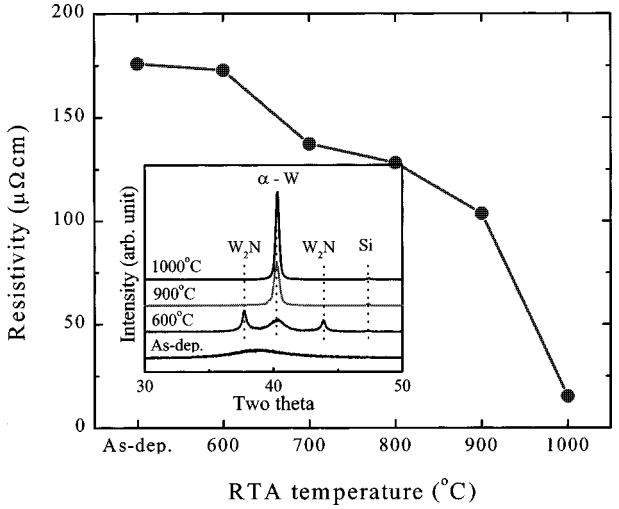

FIG. 2. X-ray diffraction spectra of $W_{67}N_{33}$ /poly-Si (inset) and resistivity as a function of RTA temperature in nitrogen for 1 min.

phase of the WN_x film as a function of the nitrogen content in the as-deposited films. The resistivity of the WN_x films increased gradually with increasing nitrogen content up to about 10%, and then leveled off with further increments of nitrogen content by 45%. With further increments of nitrogen content, above 45%, the resistivity of the WN_x films was drastically increased. In the case of 10%–45% of nitrogen content, the as-deposited WN_x was an amorphous structure, as shown in the inset of Fig. 1. To the contrary, the WN_x films containing 50% of nitrogen were polycrystalline. Affolter reported that the amorphous WN_x film containing 33% of nitrogen was easily crystallized into W_2N during vacuum annealing at 600 °C for 30 min.[11] Also, this WN_x film deposited on SiO_2 was transformed to a low-resistive α-phase W by annealing at 800 °C for 30 min, while the polycrystalline WN_x film containing 50% of nitrogen was not completely transformed to the α-phase W, even after annealing at 800 °C. Therefore, WN_x films composed of $W_{67}N_{33}$ were used in this work.

Figure 2 shows the resistivity of the $W_{67}N_{33}$ film on poly-Si as a function of RTA temperatures. The resistivity of

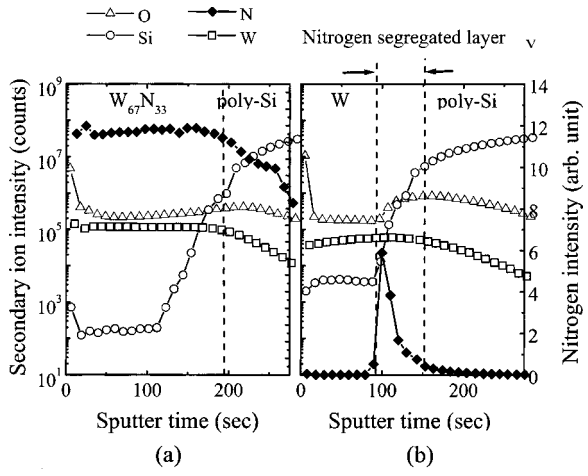

FIG. 3. SIMS depth profiles of $W_{67}N_{33}$ on a poly-Si substrate: (a) as-deposited and (b) after RTA at 1000 °C. The intensities of nitrogen were normalized by an intensity of (a) tungsten and (b) silicon indicated on the right-hand axis.

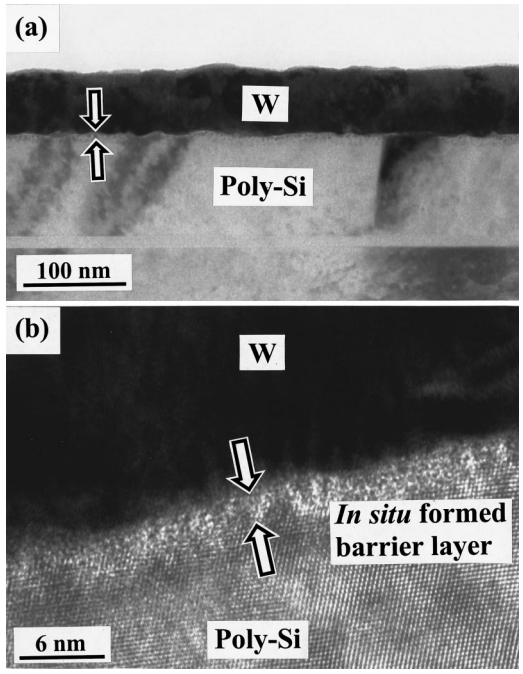

FIG. 4. TEM micrograph of $W_{67}N_{33}$ on poly-Si after RTA at 1000 °C for 1 min: (a) uniform interface of a W/poly-Si structure and (b) amorphous layer between W and poly-Si.

the as-deposited film was 175 $\mu\Omega$ cm and decreased with higher RTA temperatures. After RTA at 1000 °C for 1 min, the resistivity was lowered to 15 $\mu\Omega$ cm, which is comparable to the value of the sputtered W, 13 $\mu\Omega$ cm. As can be seen in the inset of Fig. 2, the amorphous structure of the as-deposited $W_{67}N_{33}$ films transformed to W_2N and α-phase W after RTA at 600 °C. As the RTA temperature was increased to 900 and 1000 °C, W_2N peaks disappeared and a new peak of α-phase W appeared. Also, higher RTA temperatures yielded a higher peak intensity of α-phase W. Therefore, we may insist that a lower resistance of $W_{67}N_{33}$ on poly-Si by RTA is mainly caused by the transformation of amorphous WN_x films to α-phase W.

It is well known that W reacts easily with Si at temperatures above 600 °C, resulting in the formation of WSi_x.[7,8] However, it is interesting to note that we were not able to

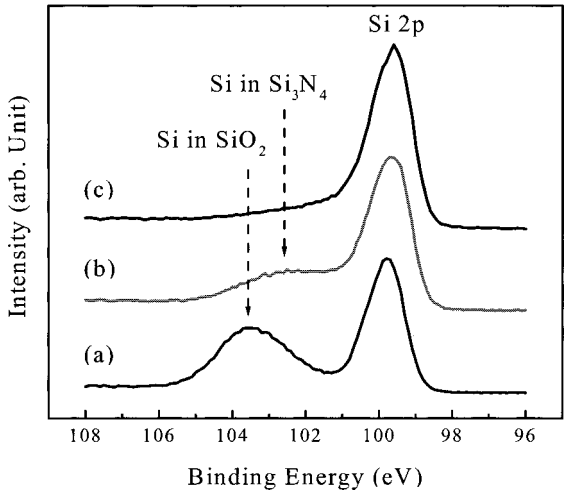

FIG. 5. XPS spectra of $W_{67}N_{33}$ on poly-Si after annealing at 1000 °C: (a) as-received, (b) after sputtering for 5 s, and (c) after sputtering for 10 s.

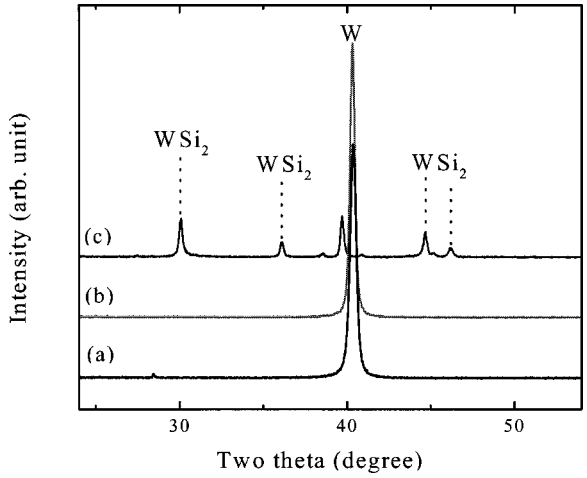

FIG. 6. X-ray diffraction spectra of the rapidly thermal annealed $W_{67}N_{33}$/poly-Si structure after hydrogen annealing at temperatures of (a) 850, (b) 1000, and (c) 1050 °C for 2 min.

observe any peaks on WSi_x with the samples tested, even after high-temperature annealing at 1000 °C (Fig. 2). To investigate the causes of the lack of formation of WSi_x, the behavior of nitrogen was investigated using SIMS analysis. Equilibrium solubility of nitrogen in W is about 10^{-3} at. % at 1000 °C. This indicates that excessive nitrogen in the $W_{67}N_{33}$ films may be diffused out and also redistributed after RTA at 1000 °C.

Figure 3 shows the SIMS depth profiles of tungsten, oxygen, silicon, and nitrogen before and after RTA at 1000 °C for 1 min. The intensities of nitrogen were normalized by the intensity of tungsten and silicon on the right axis. In the case of the as-deposited film, the concentration of nitrogen was uniformly distributed in depth, but after RTA at 1000 °C, most of the nitrogen atoms were dissipated and partially segregated at the W/poly-Si interface, as in Fig. 3(b). To evaluate the characteristics at the interface of the WN_x and poly-Si, TEM analysis was conducted with the sample annealed at 1000 °C. As shown in Fig. 4(a), the interface of W and poly-Si was extremely uniform and there was no layer of WSi_x. The nitrogen-segregated layer is clearly seen in the high-resolution TEM photograph in Fig. 4(b). The thickness of the segregated layer was about 2 nm and the structure was amorphous. From the analysis results of SIMS and TEM, it may be concluded that the segregated layer acts as a barrier protecting any interaction between W and poly-Si, even at such a high RTA temperature of 1000 °C.

In order to identify the chemical bonding status of the segregated layer, XPS analysis was performed (Fig. 5). To avoid the ''interface effect'' at the interface of W and poly-Si, the W layer was removed using a boiling H_2O_2 solution, before XPS analysis. Before sputtering the surface of the sample, a strong peak of Si in the SiO_2 peak was detected, probably due to the oxide formed during the H_2O_2 treatment. However, a peak indicating the silicon nitride (Si–N) bonding status was clearly seen after sputtering the sample for 5 s, and a peak of pure silicon appeared with further sputtering. This result implies that the segregated nitrogen has a Si–N bonding status.

The thermal stability of the $W_{67}N_{33}$/poly-Si structure treated by RTA at 1000 °C under nitrogen atmosphere was evaluated at the annealing temperatures of 850, 1000, and 1050 °C in a hydrogen environment for 2 min. It was found that the RTA-treated $W_{67}N_{33}$/poly-Si structure was stable up to 1000 °C for 2 min annealing, as shown in Fig. 6, due to the nitrogen-segregated layer acting as a barrier between W and poly-Si.

In summary, the structure of $W_{67}N_{33}$/poly-Si converted into α-phase W/nitrogen-segregated layer/poly-Si layers by RTA at 1000 °C for 1 min. The α-phase W layer was used as a low-resistive electrode, and the nitrogen-segregated layer at the interface of W/poly-Si acted as an *in situ* formed diffusion barrier, which successfully suppressed the silicidation between W and poly-Si. The nitrogen-segregated layer was an amorphous structure and revealed a Si–N bonding status.

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