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Charging characteristics of Ru nanocrystals embedded in Al₂O₃ matrix prepared by using the initial growth stage of Ru plasma-enhanced atomic layer deposition

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Ru nanocrystal layers were successfully prepared on the Al₂O₃/Si substrate by controlling the initial growth stage of Ru plasma-enhanced atomic layer deposition (PE-ALD). The spatial density and average size of the Ru nanocrystals were carefully controlled by the number of deposition cycles during the Ru PE-ALD. When the number of deposition cycles reached 60, the maximum spatial density and average diameter of Ru nanocrystals were 2.5×10^{12} cm⁻² and 3.8 nm, respectively. In order to measure the electrical characteristics of the nanocrystal floating-gate memory, a metal–oxide–semiconductor (MOS) structure (p-type Si/Al₂O₃/Ru nanocrystal layer/Al₂O₃/Pt) was fabricated without breaking the vacuum. The capacitance-voltage measurement of the MOS structure revealed that the incorporation of a Ru nanocrystal layer resulted in a large flatband voltage shift (4.1 V) at a sweep range of -5 to 5 V, which corresponds to a charge spatial density of 1.22×10^{-6} C/cm². Therefore, the initial stage of Ru PE-ALD can potentially be exploited for next-generation floating-gate memory cells.

Key words: Ruthenium, Nanocrystal, PE-ALD, Initial growth stageIntroduction.

Introduction

Nonvolatile memory devices have been extensively studied because their small dimensions and low power consumption make them easily portable [1, 2]. Since the first report of a floating-gate (FG) nonvolatile semiconductor in 1967 [3], the concept of FG memory has been considered as a crucial factor in nonvolatile electronic storage device research [4]. However, in spite of recent progress in this area, conventional FG devices possess inherent limitations related to the continuous scaling of the device structure. In conventional FG devices, this scaling limitation stems from the necessary requirement of a thin tunnel oxide layer for isolating the FG [5, 6]. The tunnel oxide layer should provide superior isolation under retention and disturbed conditions in order to maintain information integrity over time periods of up to a decade. At the same time, the tunnel oxide should allow for quick and efficient charge transfer to and from the FG [5]. To improve the isolation of the FG, the thickness of the tunnel oxide should be increased; however, to improve the device speed, the thickness of there is a necessary tradeoff between speed and reliability that is related to the thickness of the tunnel oxide (measured to about 8-11 nm) [6]. To overcome this limitation in conventional FG memory,

the tunnel oxide is required to be reduced. Therefore,

nanocrystal FG memory, in which one uses continuous thin films, is of particular interest. In nanocrystal FG memory, charge is stored in the electrically isolated nanocrystals. Therefore, the local leakage paths will not cause whole charge loss. Nanocrystal memory has better retention characteristics than conventional FG memory, which therefore allows the use of a reduced tunnel oxide thickness [5]. For this application to be successful, the fabrication method for the nanocrystal layers needs to be carefully considered so that a high spatial density and uniform size of nanocrystal can be obtained. A high spatial density of nanocrystals can enhance the charge storing capability of the floating layer, and a uniform size of nanocrystals can ensure reproducible storage characteristics [4]. Recently, it has been reported that Ru nanocrystal layers with a high spatial density and uniform-sized nanocrystals, can be obtained by controlling the initial growth stage of Ru plasmaenhanced atomic layer deposition [7]. Ru has a high work function (4.7 eV), and therefore Ru nanocrystals can provide good retention and charging characteristics,

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which in turn makes them useful for nanocrystal FG memory applications.

In this study, we have investigated the charging characteristics of Ru nanocrystal layers that were prepared using the initial growth stage of Ru plasmaenhanced atomic layer deposition (PE-ALD). In order to obtain maximum spatial density with uniform size distribution of Ru nanocrystals, the tunnel oxide material and the deposition cycle of the PE-ALD were carefully controlled. Moreover, the electrical properties of the metal-oxide-semiconductor (MOS) structure with embedded nanocrystals were investigated by measuring the corresponding current-voltage (C-V) curve.

Experimental

Ru nanocrystal layers were grown on SiO₂/Si and Al₂O₃/Si substrates using the deposition techniques of atomic layer deposition (ALD) and PE-ALD. For the Ru ALD, bis (ethylcyclopentadienyl)-ruthenium [Ru(EtCp)₂] and oxygen gas (O₂) were used as a Ru precursor and reactant, respectively. For the Ru PE-ALD, ammonia (NH_3) plasma was used as a reactant instead of O_2 gas. Detailed experimental conditions of Ru PE-ALD and ALD have been described elsewhere [7, 8]. In a converged region, the growth rate of Ru ALD and Ru PE-ALD were 0.1 nm/cycle and 0.038 nm/cycle, respectively. As a tunnel oxide and blocking oxide layer, Al₂O₃ thin films were deposited by ALD at a deposition temperature of 250 °C and deposition pressure of 1 torr. Trimethylaluminum [Al(CH₃)₃] and isopropyl alcohol (IPA) were used as the Al precursor and reactant, respectively [9]. The growth rate of Al₂O₃ was 0.08 nm/ cycle. To investigate electrical properties, the MOS structure (p-Si(100)/Al₂O₃/Pt) with Ru nanocrystal was fabricated by the following procedure: Before forming the tunnel oxide, Si wafer was etched in buffered HF to remove any native oxide before being rinsed in deionized water. After depositing 6-nm-thick Al₂O₃ tunnel oxide by ALD, a layer of Ru nanocrystal was formed by PE-ALD. Subsquently, 19-nm-thick Al₂O₃ blocking oxides were deposited on the Ru nanocrystal layer by ALD. Finally, a Pt top electrode was deposited using the sputtering technique. All the processes described for preparing the MOS structure were performed without breaking the vacuum. In order to minimize charge trapping within the Al₂O₃ layer, after deposition, the annealing process was carried out using a rapid thermal annealing (RTA) system under an ambient N₂ atmosphere at 400 °C, for 30 min.

The size and spatial density of the Ru nanocrystal were analyzed by field emission scanning electron microscopy (FE-SEM, Hitachi S4800) and transmission electron microscopy (TEM, Philips F20). The charging characteristics of the MOS structures were investigated by capacitance-voltage (C-V) measurements at a frequency of 1 MHz using a multifrequency LCR meter (Keithley 590 CV analyzer). The scanning step and scanning speed were fixed at 0.1 V and 10 steps per second, respectively.

Results and Discussion

Fig. 1 shows SEM images of Ru nanocrystals prepared by (a) ALD and (b) PE-ALD on the Al₂O₃/Si substrate. The number of deposition cycles was fixed at 30. When conventional ALD was used, the Ru nanocrystals had a low spatial density with a non-uniform size distribution (Fig. 1(a)). However, Ru nanocrystals prepared by PE-ALD had a high spatial density with a uniform size distribution (Fig. 1(b)). These differences were caused by the difference between the initial stage of Ru-ALD and that of PE-ALD. For example, in the initial stage of ALD, the strong preferential growth of Ru on the homogenous Ru nuclei is significant, which means that the Ru nanocrystals grow faster on Ru nuclei than on Al₂O₃ substrate. On the other hand, the preferential growth of Ru in PE-ALD is very weak, as has also been reported previously [7]. Therefore, PE-ALD is more





Fig. 1. SEM images of (a) Ru ALD and (b) Ru PE-ALD deposited on an Al_2O_3/Si substrate. The number of deposition cycles was fixed at 30.



Fig. 2. SEM images of Ru PE-ALD prepared on (a, b, c) SiO₂/Si substrate and (d, e, f) Al_2O_3 /Si substrate, with various numbers of deposition cycles: (a, d) 10, (b, e) 20 and (c, f) 30 cycles.



Fig. 3. Plan-view TEM images of Ru nanocrystals prepared by PE-ALD on Al₂O₃/Si substrate with various numbers of deposition cycles.

suitable than ALD for preparing Ru nanocrystals with a higher spatial density. In general, the initial stages of PE-ALD are strongly influenced by the initial substrate material. Therefore, in this work, Ru nanocrystals were prepared by PE-ALD on the SiO₂/Si and Al₂O₃/Si substrates in order to investigate the effect of substrate materials on the spatial density of the Ru nanocrystals. Fig. 2 shows SEM images of Ru nanocrystals prepared on SiO₂/Si and Al₂O₃/Si substrates with various numbers of deposition cycles. By increasing the number of PE-ALD cycles, the spatial density and average size of the Ru nanocrystals increased. It can also be seen from the PE-ALD data that for an equal number of cycles, the spatial densities of Ru nanocrystals prepared on an Al₂O₃/Si substrate are higher than that on a SiO₂/Si substrate. This phenomenon can be explained by the number of terminal OH groups on the two substrates. It is known that the maximum density of hydroxyl (OH⁻) groups on an Al₂O₃ surface is about two times higher than those on a SiO_2 surface [10]. Since such hydroxyl groups can act as precursor chemisorption sites, a high density of OH termination seems to result in a high spatial density of Ru nanocrystals.

To carefully investigate the spatial density of the Ru nanocrystals that were prepared by PE-ALD, TEM analysis was performed with various numbers of deposition cycles. Fig. 3 shows the plan-view TEM image of the Ru nanocrystals prepared by PE-ALD on an Al_2O_3/Si substrate with different deposition cycles. The corresponding spatial density and average Ru



Fig. 4. The spatial density and average size of Ru nanocrystals with various numbers of deposition cycles.

nanocrystal size are shown in Fig. 4. By increasing the number of deposition cycles from 20 to 60, the spatial density and the average size of the Ru nanocrystals also increased. The maximum nanocrystal spatial density of 2.5×10^{12} cm⁻² and average nanocrystal diameter of 3.8 nm were obtained at the deposition cycle of 60. However, a further increase in the number of deposition cycles from 60 to 100 caused a gradual decrease in the spatial density of the Ru nanocrystals due to coalescence between nanocrystals, as shown in Fig. 3(d) and (e). Considering the concept of nanocrystal FG memory, it is important to ensure electrical isolation between nanocrystals. Therefore, such coalescence phenomena



Fig. 5. Cross-sectional TEM images of MOS structure.



Fig. 6. Capacitance-voltage (C-V) hysteresis curve of MOS structure (a) with and (b) without Ru nanocrystal.

need to be avoided.

Fig. 5 shows the cross-sectional TEM images of MOS structures with Ru nanocrystal layers that were prepared by PE-ALD (60 deposition cycles) in order to measure the electrical properties. The detailed sequence of fabrication for this MOS structure was described in

the experimental section. The thickness of the tunnel oxide, Ru nanocrystals, and blocking oxide layers were controlled to 6.0, 3.5 and 19 nm, respectively. From Fig. 5, a very thin (ca. 0.5 nm) amorphous interfacial layer between the Si and Al_2O_3 tunnel oxide layers was found to be an aluminum silicate ($Al_xSi_yO_z$) layer, which is inevitably formed upon PE-ALD. Ru nanocrystals were mostly spherical in shape with a narrow size distribution (in the range 3-5 nm) and were well isolated within the Al_2O_3 layer. For this structure, the Pt electrode was deposited using the sputtering method.

Fig. 6 shows the capacitance-voltage (C-V) curves measured at 1 MHz using the MOS structure (a) with and (b) without Ru nanocrystals. The voltage step was 0.1 V and the voltage sweeping speed was 10 steps per second. When the voltage was applied to the Pt electrode, a narrow C-V hysteresis was observed when there was no Ru nanocrystal layer (Fig. 6(a)). A very small flatband voltage shift of 0.4 V was observed with a sweep range of -5 to 5 V. This would appear to have originated from the oxide trap charges or mobile ions in the Al₂O₃ layer. On the other hand, a very large C-V hysteresis was observed when a Ru nanocrystal layer was present (Fig. 6(b)). The flatband voltage shift increased with an increase in the voltage sweep range in the C-V measurement. With a voltage sweep range of -5 to 5 V, a very large flatband voltage shift of 4.1 V was obtained. The amount of charge stored in the Ru nanocrystal layer can be calculated by using the following equation:

$$\Delta V_{FB} = \Delta Q / C_{OX} \tag{1}$$

where ΔV_{FB} is the flatband voltage shift, ΔQ is the amount of stored charge per unit area, and C_{OX} is the capacitance of the blocking oxide layer per unit area. From C-V analysis, C_{OX} of the blocking oxide layer was measured to be 3.38×10^{-7} F/cm². The flatband voltage shift that originated from the Ru nanocrystal layer (3.7 V) was calculated by subtracting the flatband voltage shift without a Ru nanocrystal layer (0.4 V) from the flatband voltage shift when a Ru nanocrystal layer is present (4.1 V). Therefore, the amount of stored charge per unit area (ΔQ) was calculated to be 1.25×10^{-6} F/ cm². The average number of stored electrons within one Ru nanocrystal was estimated from the spatial density of the Ru nanocrystal layers by the following equation:

$$N_e = \Delta Q / (q N_{\rm NC}) \tag{2}$$

where Ne is the number of stored electrons, N_{NC} is the spatial density of the Ru nanocrystal layer, q is the charge of an electron (-1.6 × 10⁻¹⁹ C), and N_e is the average amount of stored charge in one Ru nanocrystal. From Fig. 3 and 4, N_{NC} was calculated to be 2.5×10^{12} cm⁻². Therefore, the average number of stored electrons in one Ru nanocrystal was calculated to be approximately 3.

Conclusions

Ru nanocrystal layers were successfully prepared by PE-ALD on an Al₂O₃ tunnel oxide layer formed on a Si substrate, using the initial stages of Ru PE-ALD. The spatial density and average size of the Ru nanocrystals were controlled by the number of deposition cycles used in the PE-ALD. When the number of deposition cycles reached 60, maximum spatial density $(2.5 \times 10^{12} \text{ cm}^{-2})$ of the Ru nanocrystal laver was achieved with an average Ru nanocrystal diameter of 3.8 nm. Capacitance-voltage measurements of the MOS structure revealed that incorporation of a Ru nanocrystal layer resulted in a large flatband voltage shift of 4.1 V at a sweep range of -5 to 5 V, which corresponds to a charge spatial density of 1.22×10^{-6} C/cm². As a consequence, the initial stages of Ru PEALD can be potentially utilized for nextgeneration floating-gate memory cells.

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