Structural and Optoelectronic Properties of a-SiO$_x$:Ag Films Used for Ag/SiO$_x$/$p$-Si Memristor

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Abstract. Silicon based memristor has attracted much attention due to its potential applications not only in electrical storage but also in electro-optical modulator. No matter what applications are mentioned, the device performance is closely related to the characters of the materials used. In this paper, a-SiO$_x$:Ag thin films are deposited on quartz substrates by co-sputtering, and their microstructural and optoelectronic properties are investigated by using XRD, Raman and ellipsometry, respectively. Finally, a memristor with Ag/a-SiO$_x$/p-Si structure is fabricated successfully, and the “ON/OFF” performance of resistivity is measured by voltammetry. The results show that a-SiO$_x$ is a potential alternate of insulator layer in the system of “Ag/insulator or semiconductor/p-Si” memristors which could be used in optical modulators in the near future.

1. Introduction
Memristor has been paid much attention in microelectronic field as a promising candidate for the next-generation nonvolatile memory with excellent miniaturization potential, high on/off ratio, fast programming speed and high-endurance[1–3]. Generally, a memristor comprises metal/insulator/metal or metal/semiconductor/metal sandwich structure. The operating principle is resistance switching between high and low states under different excitation voltages. The switching of resistance is realized by metal filament formation (or dissolution) in the insulator (or in the semiconductor) at positive (or negative) applied voltage. During this resistance switching procedure, optical properties of the insulator (or semiconductor) could be adjusted as well, making the optical application of memristors potentially possible. Given that compatibility of the fabrication with complementary metal oxide-semiconductor (CMOS) technology, Si-base materials are the best choice for the insulator (or semiconductor). Recently, Emboraset al[4–5] demonstrated experimentally that a new optical switch with atomic sizes and low power consumption can be realized by incorporating memristor with Ag/a-Si/p-Si (p-typesilicon) structure into an optical waveguide. In the new optical switches, the p-Si substrate acts as Si waveguide and the a-Si dielectric layer acts as cladding layer both in an optical waveguide, respectively. Thus the propagating light in the waveguide would be modulated due to the optical property switching of the dielectric layer during switching process. Although the optical switching based on memristor has already been realized [6], the principle behind the device is still unclear up to now.

Concerned about a new optical switch based on memristor, SiO$_x$ is a better alternate than a-Si.
memistor based on SiOx has some unique characteristics. More importantly, SiOx is more suitable than a-Si used as cladding layer of an optical waveguide due to its lower refractive index, and it is well known that silicon oxide (SiOx) has been widely used as the cladding layer of optical waveguide. Accordingly, the performance of the optical switch based on SiOx might be expected to have a surprising improvement.

In addition, device performance is closely related to the characters of the materials used. It is noted that several literatures have investigated the surface plasma resonance and optical absorption of SiOx:Ag thin films [7-8]. So, for Ag/SiOx/p-Si memristor, the SiOx layer consisting of silver filament could be seen as a kind of SiOx thin film embedded with Ag nanoparticles, and the study of silicon oxide alloyed by silver (SiOx:Ag) thin film will help us to well understand the optoelectronic properties of SiOx memristor.

In this paper, a-SiOx:Ag thin films are prepared by co-sputtering method, and the structural, optoelectronic properties of the thin films are characterized by using XRD, Raman, voltammetry and ellipsometry methods, respectively. Finally, a memristor with Ag/a-SiOx/p-Si structure is fabricated and the resistivity ON/OFF behaviour is studied based on I-V measurement.

2. Experimental Procedure

The a-SiOx:Ag thin films were deposited on the quartz substrates by RF magnetron co-sputtering. The chamber was pumped to a base pressure of 7×10⁻⁴ Pa and the substrates were heated to 250°C before deposition. The RF power was set to 200 W. Argon (Ar) flow served as working gas was kept at 200 sccm to keep the chamber pressure in 0.5 Pa. At the same time, oxygen (O₂) flow was kept at 3 sccm as the reaction gas during sputtering. To introduce Ag atoms, several Ag chips (99.99%) were fixed on the Si target (99.999%) and H₂ flow was not introduced here. The nominal Ag concentration, varying from 0.8% to 6.4%, was estimated by the target coverage proportion of Ag chips and the sputtering yields. Panalytical X’pert HighScore XRD instrument was applied to measure the X-ray diffraction spectra, in which a conventional CuKα radiation (λ=1.5418Å) was used, and the angle of incidence was set at 1°. The amorphous network of a-SiOx:Ag thin films were analysed by a RENISHAW inVia Raman Microscope at a wavelength of 514 nm. The power was set below 5 mW to avoid laser-induced crystallization. Optical constants of the a-SiOx:Ag thin films were extracted by SENTECH SE850 ellipsometer. The film resistivities were measured by a Keithley 6517A semiconductor characterization system (SCS). Finally, a memristor made of Ag/SiOx/p-Si was fabricated and the I-V performance was carried out by a Keithley 4200 AS CS.

3. Results and Discussion

Figure 1 shows the XRD spectra of a-SiOx:Ag thin films with different Ag concentrations. The four peaks belong to Ag nanocrystals including 38.4° assigned to Ag (111), 44° assigned to Ag (200), 65° assigned to Ag (220) and 77° assigned to Ag (311) with Ag concentration at about 6.4%, respectively. For samples with lower Ag concentrations (3.2% and 1.6%), only single peaks of Ag (111) are observed, but when Ag concentration is lower than 1.6%, this typical peak can not be found in XRD spectra. This could be explained by the detection limit of XRD method owing to the relatively low fraction of Ag nanocrystals. Mean sizes of Ag nanocrystals could be calculated by Scherrer formula and the relationship between mean grain size and Ag concentration is shown in the insert of Figure 1. It can be seen that when the Ag concentration is increased from 1.6% to 6.4%, the Ag nanocrystal size goes up from 1.48 nm to 2.43 nm. These sizes are close to those of Ag nanoparticles formed in the Ag/SiOx/Pt memristor [9].
Figure 1. XRD spectra of SiOx:Ag films and mean size of nanocrystals with Ag concentration.

Figure 2(a~d) shows Raman spectra and the variations of the testing thin films with Ag concentration. It can be seen that these Raman spectra are typical forms of amorphous semiconductor materials. As shown in figure 2(b) and (c), when Ag concentration increases from 0 to 6.4%, the transverse optical peak ($\omega_{\text{TO}}$) shifts from 492.5 cm$^{-1}$ to 450.7 cm$^{-1}$ and the peak width $\Gamma_{\text{TO}}$ increases from 52.4 cm$^{-1}$ to 92.6 cm$^{-1}$, indicating that a-SiOx:Ag thin films present a large short-range disorder with the increase of Ag concentration [10-11]. From figure 2(d), one can see that the $I_{\text{TA}}/I_{\text{TO}}$ ratios increase from 0.63 to 1.66 with the increase of Ag concentration, implying a more disorder amorphous network in medium-range.

Figure 3(a) shows the resistivity variation of a-SiOx:Ag thin films with different Ag concentrations. It can be seen that with the increase of Ag from 0 to 6.4%, the resistivity decreases from $\sim 10^6$ ($\Omega$.cm) to $10^{-1}$ ($\Omega$.cm), which spans almost 7 orders of magnitude. The metallic conducting tunneling formed by Ag nanocrystals could be responsible for this large gap of resistivity. And this gap is large enough to cover the range between On and Off states of an Ag/a-SiOx/p-Si memristor. In order to gain more insights into the resistance switching behavior of an Ag/a-SiOx/p-Si memristor, we have measured the I-V characteristics of this memristor as shown in figure 3(b). The bias voltage is applied to the top metal (Ag), while the back contact (p-Si) is grounded, and the area of Ag electrode is about 1mm$^2$. A high on/off ratio is observed from the I-V curves. When the voltage is increased above a threshold voltage, the memristor is turned on and the conductance is increased very rapidly. It can be seen that the current increases from $\sim 10^{-8}$ A to $10^{-3}$ A, which spans almost 5 orders when the bias
voltage exceeds the threshold voltage. This switching behavior is attributed to the formation of silver filament as in Ag/a-Si/p-Si memristor [12-13]. It is considered that when the memristor is turned ON at a positive applied voltage, Ag cations migrate into a-SiO\textsubscript{x} layer, and the layer could be taken as a kind of a-SiO\textsubscript{x} thin film embedded with Ag nanoparticles. Therefore, the large variation in resistivity of a-SiO\textsubscript{x}:Ag thin films might be related to the result that the experimental Ag/a-SiO\textsubscript{x}/p-Si memristor exhibits over 5 orders of On/Off ratio. The switching threshold voltage and the compliance current observed in the present study are 3.2V and 1mA, respectively, which are almost equal to the values of Ag/a-Si/p-Si memristor published elsewhere [14]. Another point needs to pay attention is the repeatability. It can be seen in Figure 3(b), moreover, that in the first circle, the On/Off ratio reaches 5 orders, while after 10th circle, the On/Off ratio decreases to less than 3 orders. This unsatisfactory repeatability can be attributed to the limits of manufacturing conditions in the fabrication of Ag/a-SiO\textsubscript{x}/p-Si memristor.

Figure 3. Resistivity of SiO\textsubscript{x}:Ag film with Ag concentration (a) and I-V curves of Ag/SiO\textsubscript{x}/p-Si memristor (b).

Figure 4 shows the dispersion relations about the refraction index and the extinction coefficient of a-SiO\textsubscript{x}:Ag thin films with different Ag concentration. As shown in Figure 4(a), one can see that changes of sliver concentration have an obviously effect on the variation of refraction index. The refraction index exhibits anomalous dispersion characteristics as the wavelength increases from 300 nm to 580 nm, but exhibits normal dispersion characteristics from 580 nm to 800 nm. This anomalous dispersion characteristic is due to the fact that resonant oscillation of the conduction electrons would be replaced by the single electron transitions of silver nanocrystals [15-16]. In the normal dispersion range from 580 nm to 800 nm, the refraction index increases with silver concentration. As shown in Figure 4(b), the extinction coefficient increases with the increase of Ag concentration. Given a pure a-SiO\textsubscript{x} film, the refraction index is much lower than that of c-Si, the transmission light can be confined inside the Si waveguide, if a nana-SiO\textsubscript{x} film is used as the cladding layer of Si waveguide. More importantly, the refraction index of a-SiO\textsubscript{x}:Ag thin film develops the increase of Ag concentration, which means that the optical parameters of a-SiO\textsubscript{x} thin film could be heavily adjusted by introducing Ag nanoparticles into the a-SiO\textsubscript{x} thin films. These interesting results imply that SiO\textsubscript{x} is a potential alternate of a-Si as in Ag/a-Si/p-Si memristor to realize an applicable optical switch.
Figure 4. Refraction index (a) and extinction coefficient (b) of a-SiOx:Ag thin films with Ag concentration. The inset of (a) shows the n values at λ=633 nm.

4. Conclusions

In summary, a-SiOx:Ag thin films are deposited by co-sputtering method, and the structural, optoelectronic properties of the thin films are characterized by using XRD, Raman and ellipsometry, respectively. A memristor with Ag/a-SiOx/p-Si structure is fabricated and the I-V curves are measured. Ag nanocrystals are successfully embedded in a-SiOx and the sizes of them are close to those of nanoparticles formed in the Ag/a-Si/Pt memristor. With the increase of Ag concentration, the amorphous network of the Ag/a-SiOx:Ag films exhibits an increase in short-range disorder and a decrease in medium-range order. The resistivity of the Ag/a-SiOx:Ag films decreases from ~10^6 (Ω·cm) to 10^1 (Ω·cm) with the increase of Ag concentration, which is high enough to cover the gap between ON and OFF states in the Ag/a-SiOx/p-Si memristor. Our recent research on the dispersion relation of a-SiOx:Ag thin films demonstrates that a-SiOx film is a potential alternate of insulator layer in the system of “Ag/insulator or semiconductor/p-Si” memristors which could be used in optical modulators in the near future.

5. References

[1] Schindler C, Weides M, Kozicki M N and Waser R 2008 J. Applied Physics Letters 92 122910.
[2] Huang R, Zhang L, Gao D, Pan Y, Qin S, Tang P, Cai Y and Wang Y 2011 J. Applied Physics A 102 297-311.
[3] Dong Y, Yu G, McAlpine M C, Lu W and Lieber C M 2008 J. Nano Letters 8 386-391.
[4] Emboras A, Goykhman I, Desiatov B, Mazurski N, Shappir J and Levy U 2013 J. Nano Lett 13 6151-5.
[5] Emboras A, Niegemann J, Ma P, Haffner C, Pedersen A, Luissier M and Hafner C 2016 J. Nano Lett 16 709-14.
[6] Li D, Guo A and Song Q 2016 J. Proceedings of the Spie 191001909.
[7] Gürer S, Budak S, Gibson B and Ilia D 2014 J. Applied Surface Science 310 180-183.
[8] Ye YH, Jiang YW, Tsai MW, Chang YT, Chen CY, Tzuo DC, Wu YT and Lee SC 2008 J. Applied Physics Letters 93 033113.
[9] Yang Y, Gao P, Gaba S, Chang T, Pan X and Lu W 2012 J. Nat Commun 3 732.
[10] Wei W, Xu G, Wang J and Wang T 2007 J. Vacuum 81 656-662.
[11] Guo A, Li W, Jiang X, Wang C and Jiang Y 2015 J. Journal of Raman Spectroscopy 46 619-623.
[12] Jo S H and Lu W 2008 J. Nano letters 8 392-397.
[13] Jo S H, Kim K H and Lu W 2009 J. Nano Letters 9 870-874.
[14] Liu Y, Gao P, Jiang X, Bi K, Xu H and Peng W 2014 J. Applied Physics Letters 104 043502.
[15] Roy R K, Mandal S K, Bhattacharyya D and Pal A K 2003 J. The European Physical Journal B - Condensed Matter 34 25-31.
[16] Guo A, Li D, Li W, Gu D, Jiang X and Jiang Y 2016 J. Materials Letters 185 5-8.