Gold nanoresistors with near-constant resistivity in the cryogenic-to-room temperature range

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ABSTRACT

Using a multiple plasma deposition-annealing (MDA) technique, we have fabricated an Au nanoisland-based thin film nanoresistor with a very low temperature coefficient of electrical resistivity in a cryogenic-to-room temperature range of 10 to 300 K. The nanoislanded gold film was deposited on a SiO$_2$/Si wafer (500 nm SiO$_2$ thickness) between two 300 nm thick Au electrodes which were separated by 100 μm. A sophisticated selection of the thickness of the nanoislanded gold film, the annealing temperature, as well as the number of deposition/annealing cycles resulted in the fabrication of a nanoresistor with a temperature coefficient of electrical resistivity of $2.1 \times 10^{-3} \text{K}^{-1}$ and the resistivity deviation not exceeding 2% in a cryogenic-to-room temperature range. We have found that the constant resistivity regime of the nanoisland-based thin film nanoresistor corresponds to a minimized nanoisland activation energy (approximately 0.3 meV). This energy can be minimized by reducing the nearest neighbor distance and increasing the size of the Au nanoislands in the optimized nanoresistor structure. It is shown that the constant resistivity nanoresistor operates in the regime where the thermally activated electron tunneling is compensated by the negative temperature dependence of the metallic-type conductivity of nanoislands. Our results are relevant to the development of commercially-viable methods of nanoresistor production for various nanoelectronics-based devices. The proposed MDA technique also provides the opportunity to fabricate large arrays of metallic nanoparticles with controllable size, shapes and inter-nanoparticle gaps.
I. Introduction

Thin-film nanoresistors (TFNRs) have many interesting features that make them among the most important components in low-temperature, high-precision, and low-power electronics. The TFNRs are vital components in biosensors, nanolasers, solar cells, plasmonic, optics, and chemosensing devices, thin film transistors, monolithic microwave integrated circuits, light emitting diodes, and many other devices. In these applications, TFNRs should demonstrate highly-controllable resistivity-temperature dependence and, for some specific devices such as high-precision/low-noise amplifiers and low-temperature nanoelectronic devices based on single-electron transistors, very stable (temperature-independent) resistivity is required. The electrical resistivity and resistivity-temperature behavior of such nanoresistors is mainly determined by their internal structure.

Thin-film nanoresistors can be fabricated using various compositions of metals and semiconductors. Recent progress in plasma-based techniques has made it possible to fabricate TFNRs using magnetron targets of appropriate composition. Moreover, the thickness and structure of the deposit can be controlled by various process parameters such as the surface bias, gas pressure, and discharge current. However, these techniques demonstrate a low controllability of the structure of nanoislanded thin films. The plasma- and microplasma-based methods also show relatively poor controllability.

To achieve a temperature-independent electrical resistivity of the TFNR, it is essential to minimize the activation energy of metallic nanoparticles (MNPs) in the nanoresistor. Generally, this can be achieved by forming dense arrays of large metallic nanoparticles (located in close vicinity of each other) on a dielectric material. In this case, precise control over the size, shape, and position of the nanoparticles is very important. Aside from the resistivity control, these parameters of surface-grown nanoparticles are important for many other applications, such as Surface Enhanced Raman Scattering (SERS). It was shown that the shape of metal nanoparticles affects the SERS enhancement. Surface coverage by metal nanoparticles and nanoparticle size were also shown to influence the surface
effects, such as the width of the surface plasmon resonance. Thus, reliable nanofabrication techniques are required to precisely control various parameters of self-assembled nanoparticles on the surface. We have previously demonstrated that the multiple deposition-annealing (MDA) technique is a convenient and highly-controllable method to achieve this goal.\textsuperscript{30} In this full paper we show that a highly-resistive (6.5×10\textsuperscript{-5} Ω×m, nearly three orders of magnitude higher than bulk Au) thin film nanoresistor with a very low temperature coefficient of resistivity (TCR) not exceeding 2.1×10\textsuperscript{-3} K\textsuperscript{-1} can be fabricated via the MDA technique. The process involves the formation and annealing of an array of self-assembled gold nanoislands on a Si wafer covered with a 500 nm SiO\textsubscript{2} layer between two 300 nm thick Au electrodes separated by a gap of 100 μm. It is shown that the constant-resistivity regime of the nanoisland-based TFNR corresponds to the minimized (about 0.3 mV) nanoisland activation energy. This effect is attributed to the reduced nearest neighbor distance and the increased size of the nanoislands in the optimized nanoresistor structure. We also demonstrate that the constant-resistivity nanoresistor operates in the regime where the thermally activated electron tunneling is compensated by the negative temperature dependence of the metallic-type conductivity of nanoislands. The structure of the array of self-assembled gold nanoislands is characterized by optical microscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM), and is analyzed by calculating the Minkowski connectivity. The obtained results then are interpreted using the framework of the Efros-Shklovskii (ES) model.

II. EXPERIMENTAL SETUP AND PROCEDURES

The multiple deposition-annealing (MDA) process consists of the repetition of a base cycle of deposition and annealing. This cycle can be repeated several times to fabricate nanoresistors of various thickness and structures. In this process, the main control parameters are the deposition time (i.e., thickness of the nanoresistor), and the annealing temperature. As the MDA method is based on several
deposition/annealing cycles, a much higher level of controllability is ensured due to the possibility to initiate nucleation and growth of small (second- and third-generation) nanoislands between the larger ones, thus providing an effective control of the array morphology. Creation of the nanoisland array with a complex distribution function appears to be very difficult (if possible at all) by the simple annealing process.

In this work we describe the properties of four typical samples which demonstrate quite different characteristics. Thus, we demonstrate the controllability of the MDA process and the possibility to fabricate a nanoresistor with very low temperature coefficient of electrical resistivity.

The thin films of gold were deposited on SiO$_2$ substrates in DC magnetron-equipped vacuum chamber in Ar atmosphere, with a base pressure of 1 Pa and a surface bias of 50 V. The schematic of the experimental setup is shown in Fig. 1(a). The vacuum chamber was equipped with a vacuum pump, substrate table with a heating/cooling system, and a gas supply system capable of maintaining the gas pressure in the chamber during the process. An electric biasing system was used to provide a negative bias up to -1000 V on the substrate table. A photo of the plasma generated by the magnetron is shown in Fig. 1(b).

The samples were prepared on the thin-film stripes (0.8 mm length × 0.2 mm width) on a 500 nm thick SiO$_2$ layer on a Si wafer. The process began with ultrasonic cleaning of the samples in acetone for 10 min, followed by sonification in ethanol for 10 min. After that, the samples were dried using a jet of compressed nitrogen. Finally, the samples were installed in the vacuum chamber and exposed to the Ar atmosphere (1 Pa) for 10 min.

The first sample was prepared by depositing a 12 nm gold layer which was then annealed at a temperature of 343 K (70 °C) for 5 min (the base cycle). Sample 2 was made by repeating the base cycle twice to produce an 18 nm thick film, followed by annealing for 5 min. Samples 3 and 4 were produced using the same technique, with the films thicknesses of 21 and 22 nm, respectively. Thus, the base cycle was repeated twice to fabricate sample 2, thrice to fabricate the sample 3, and so forth. After
fabrication of the gold films, 300 nm thick Au contact electrodes were deposited onto the samples using a photolithography process. A schematic of the sample design and electrical measurements, as well as a low-magnification optical photo of the nanoresistor with contact electrodes are shown in Fig. 1(c) and 1(d).

All processes were conducted in a Class 100 clean room. Surface morphology of the samples was characterized by field-emission scanning electron microscopy (FESEM; Zeiss Ultraplus) and atomic force microscopy (AFM; Asylum Research MFP-3D). To analyze the morphology and connectivity of the nanoisland arrays by SEM images, we used a very low energy of the primary electrons (1 kV) to decrease the scattering by the deeper layers of the material, thus increasing the contrast between the metal and the silicon substrate. Since the penetration of electrons into metal is very shallow at low energies, and the penetration into silicon is much deeper, we have obtained SEM images of very high contrast clearly mapping the metal nanoislands and connections between them. For analyzing the arrays, we used a standard morphology analysis software supplied with the AFM system, capable of simultaneously performing the morphology and statistical analysis. The height and height distribution of the nanoparticles in the arrays was studied by the AFM technique.

All the temperature-dependent electrical resistance measurements of the samples were conducted in the temperature range from 10 to 300 K using the Physical Property Measurement System (Quantum Design Model 6000), by probing the two 300 nm thick gold electrodes. The annealing processes and the electrical measurements were carried out at a pressure of 4.1 Torr.

### III. RESULTS AND DISCUSSION

#### A. Structure of the nanoislanded gold film

We recall here that our aim was to fabricate a nanoresistor with temperature-independent resistivity in the cryogenic-to-room temperature range, and to demonstrate how the process parameters
control the electrical characteristics of the nanoisland-based nanoresistor. Thus, here we will present the results of the structure and electrical properties measurements for the four characteristic samples. Two of these samples demonstrate a near-zero temperature coefficient of resistivity $\eta$, one demonstrating a positive temperature behavior (an increase of the resistivity with temperature), and one demonstrating negative behavior.

The SEM images of the four samples of different thickness (note that the images were taken after the annealing) are shown in Fig. 2. From this figure one can see that the samples exhibit a rather complex structure, with a mix of smaller isolated nanoislands and more complex branched multilinked nanostructures. Analysis of Fig. 2 shows the two main features of the film structure. Firstly, the width-to-gap ratio $\mu$ is approximately constant within each sample, and increases from $\mu=1$ for sample 1 (12 nm) to approx. $\mu=3$ for sample 4 (22 nm). This is mainly due to the increase of the nanoisland width $\Delta$ with the film thickness (from $\Delta=25$ nm approx. for sample 1, to $\Delta=50$ nm approx for sample 4). However, the gap between nanoislands, $\delta$, becomes slightly narrower with thickness increased (from $\delta=20$ nm approx. for sample 1 to $\delta=12$ nm approx for sample 4).

Secondly, the morphology and connectivity of the film structure, i.e. the number of mutual interconnections within the film, appears to be different for each sample. In Fig. 3 we show several typical nanostructures found in samples 1 and 2. In sample 1, four main types of nanostructures are present, namely: large branchy multilinked nanoislands, small branched multilinked nanoislands, simply connected small branchy nanoislands, and rounded nanoislands. In sample 2, large branchy multilinked nanoislands, small branched multilinked islands, and simply connected branchy nanoislands are present, but no rounded nanoislands are observed. The difference in the width-to-gap ratio $\mu$ is also clearly visible.

It is quite clear that the length and connectivity of the nanostructures in the nanoresistor should directly influence the resistance. That is why we have undertaken a special study of the connectivity by calculating the Minkowski connectivity distributions,$^{31}$ which is an effective method for analyzing
various thin film morphologies and has been successfully used to study the properties of nanotube arrays.\textsuperscript{32} Figure 4 provides a 3D visualization of samples 1 (12 nm) and 2 (18 nm), and the calculated Minkowski distributions for these samples. A maximum of the distribution is shifted to the right for sample 2, thus evidencing a more interconnected structure of this sample. To compare these distributions for all four samples, we have plotted a single connectivity graph in dimensionless coordinates (Fig. 5) demonstrating the shift of the distribution with increasing film thickness and changing morphology as seen in Fig. 2. From this image one can see that sample 1 (12 nm) is characterized by the lowest connectivity (maximum at $Z/Z_{\text{max}} = 0.71$), sample 2 (18 nm) shows the highest connectivity with the maximum at $Z/Z_{\text{max}} = 0.82$; and samples 3 and 4 demonstrate intermediate values.

**B. Electrical resistivity characteristics**

Let us now examine the resistivity-temperature behavior of the four samples. In Fig. 6(a) we show an Arrhenius plot of the resistivity logarithm against the inverse temperature for samples 1, 2, and 3. All graphs contain clearly visible near-linear sections, in contrast to the samples produced by the MDA technique with high-temperature annealing,\textsuperscript{28} where a sharp kink was observed for some specimens. Moreover, all these samples demonstrate a decrease of the resistivity with increased temperature, thus the primary conductivity mechanism is thermally activated hopping introduced by Miller and Abrahams.\textsuperscript{33} The tunneling activation energy of nanoislands (electrostatic potential energy required to transfer one electron from one nanoisland to its nearest neighbor through the substrate) is plotted against the sample thickness in Fig. 6(b). It was mentioned above that the gap $\delta$ between the nanoislands is less for thicker films (i.e., samples 2 and 3). Thus, the decrease of the tunneling activation energy could be directly attributed to the morphology of the nanoresistor structure. When the activation energy is minimized to zero due to contact between nanoislands, we observe a clear transition to metallic behavior (sample 4).
In Fig. 7(a) we show the dependence of the resistance on temperature in the cryogenic-to-room temperature range for sample 4 (22 nm, four deposition-annealing cycles). The inset illustrates the same dependence for the cryogenic temperature range of 10 to 85 K. It is clearly seen from this graph that, in contrast to samples 1-3, sample 4 demonstrates a metallic type of conductivity (resistivity growth with the temperature) due to the formation of a continuous electrical path resulting from increasing the size of nanoislands and their coalescence.

The Arrhenius plot of $\ln(R)$ for all four samples in the cryogenic-to-room temperature range is shown in Fig. 7(b). One can see that samples 2 and 3 demonstrate a near temperature-independent resistivity, with the average variation not exceeding 2%.

C. Conductivity mechanisms at cryogenic and room temperatures

Thus we have experimentally shown that the morphology of the nano-islanded thin film, namely the size, thickness, shape, and connectivity of the nanoislands, dramatically changes the resistance-temperature dependencies. Specifically, the 12 nm specimen which is characterized by the lowest width-to-gap ratio $\mu \approx 1$ [see Fig. 1(a)] and the lowest Minkowski connectivity has demonstrated the inverse resistivity-temperature dependence at the ohmic region which is characteristic of the hopping mechanism. Samples 2 and 3 show a perfectly temperature-independent behavior in the cryogenic-to-room temperature range, and sample 4 shows a metallic type of conductivity.

From these observations one can draw two main conclusions. Firstly, the thin-film nanoresistors made of samples 1-4 operate in different conductivity modes. Secondly, samples 1 and 2 demonstrate a different behavior in the two temperature ranges, namely 200-300 K (Range 1), and 10-200 K (Range 2).

The transition between the two modes at the boundary of Range 1 and Range 2 is clearly seen in Fig. 7(b). It can be explained in the framework of the Efros-Schklovski (ES) model. Indeed, in the ES
model, the resistance in a low-field regime is related to the temperature as \( R_0(T) \sim \exp\left(\sqrt{T_0/T}\right) \) (here \( T_0 \) is a material-specific constant).\(^{35}\) This is why the dependence of \( \ln(R) \) on \( T^{0.5} \) is expected to be linear, as seen in Fig. 8(a). This model is valid in the low-field regime. To prove that the conditions for the low-field regime are satisfied, we have plotted the volt-ampere diagram of sample 3 that exhibits the ohmic behavior [Fig. 8(b)].

In the cryogenic temperature range 10-200 K (Range 2) samples 2 and 3 demonstrate a temperature-independent behavior. It is clear that the thermally activated tunneling, which leads to the resistance drop with increasing temperature, cannot be the dominant mechanism for electrical conduction in Range 2, and the increase of resistance may be compensated for by the metallic resistance-temperature dependence of the gold nanoislands and direct tunneling process. Since the thermally activated tunneling conductivity depends on the gaps between nanoislands, and metallic conductivity depends on the nanoisland size, the compensation of these two effects resulted in the temperature-independent behavior of samples 2 and 3. Taking into account the barrier height between two nanoislands (~1 eV for a 2.5 nm gap) we calculated the resistivity variation in the temperature range from 10 to 300 K using Simmon’s equation.\(^{36}\) This variation (of about 1.01 %) is in good agreement with the average resistivity variation obtained in the experiment (~2%).

It could be also mentioned that the resistivity-temperature dependence of our samples is quite similar to those measured for the granular metals.\(^{35}\) This is quite understandable as the intergrain resistivity also plays an important role in the conductivity of the granular structures. At the same time, the resistivity trend of the granular structures may be much more complex. In our case, as can be seen in Fig. 7(a), metallic behavior smoothly turns into a temperature-independent trend. Nevertheless, the similarity in the trends is important for better understanding the physics of the conductivity in granular structures and discontinuous films of complex morphology.

Sample 1 is characterized by thin nanoislands and wide gaps. As a result, the thermally activated tunneling conductivity behavior dominates in this case. In contrast, sample 4 consists of very wide
nanoislands with narrow gaps between them where coalescence of nanoislands occur; as a result, the thermally activated tunneling becomes less significant, and the metallic conductivity of the Au nanoislands determines the specimen behavior.

IV. CONCLUSIONS

In summary, we have demonstrated that the multiple deposition-annealing technique is effective for the fabrication of Au nanoisland-based thin film nanoresistors with a near constant resistivity in the cryogenic-to-room temperature range of 10 to 300 K. A proper selection of the process parameters and device characteristics such as the gold film thickness, number of deposition/annealing cycles and annealing temperature made it possible to fabricate a nanoresistor with the temperature coefficient of resistivity not exceeding 2.1×10^{-3} K^{-1}, which resulted in the resistivity deviation not exceeding 2%. The proposed method also provides the opportunity to fabricate large arrays of metallic nanoparticles with controllable size, shape and inter-nanoparticle gaps. Our results are relevant to the development of commercially-viable production method for nanoresistors for various nanoelectronics-based devices.

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Figure Captions

FIG. 1. (Color online) (a) Schematic of the experimental setup for deposition of nanoislanded gold films. (b) Photo of the magnetron plasma discharge in the vacuum chamber. (c) Scheme of the sample and electrical measurements. (d) Photo of the thin film nanoresistor fabricated by the MDA technique.

FIG. 2. SEM photos of the four samples of different thickness and film morphology. (a) Sample 1 – 12 nm; (b) sample 2 – 18 nm; (c) sample 3 – 21 nm; (d) sample 4 – 22 nm.

FIG. 3. (Color online) Typical nanostructures (nanoislands) found in samples 1 and 2. Panel I (sample 1, 12 nm): (a) large branchy multilinked nanoisland; (b) small branched multilinked nanoisland; (c) simply connected small branchy island; (d) rounded nanoisland. Panel II (sample 2, 18 nm): (a) large branchy multilinked nanoisland; (b) small branched multilinked island; (c) simply connected branchy nanoisland. The width-to-gap ratios $\mu$ are approximately the same for all nanoislands in the sample: $\mu \approx 1$ for sample 1, and $\mu \approx 2$ for sample 2.

FIG. 4. (Color online) 3D visualizations and Minkowski connectivities for samples 1 and 2. A maximum is shifted to the right for sample 2 (18 nm), thus demonstrating a more interconnected structure of this sample.

FIG. 5. (Color online) Comparison of the normalized Minkowski connectivities for the four samples. Sample 2 shows the maximum at the largest $Z/Z_{\text{max}}$.

FIG. 6. (Color online) (a) Arrhenius plot of the logarithm of resistance in the low-to-room temperature range, and (b) activation energy for the three samples.

FIG. 7. (Color online) (a) Temperature dependency of resistance for sample 4 in the cryogenic-to-room temperature range (inset for the cryogenic temperature range). Sample 4 demonstrates a metallic type of conductivity. (b) Arrhenius plot of $Ln(R)$ for all four samples in the cryogenic-to-room temperature range. Samples 2 and 3 demonstrate a temperature-independent resistivity coefficient. An average variation in resistance for sample 2 does not exceed 2% in the temperature range from 10 to 300 K.

FIG. 8. (Color online) (a) Dependence of $Ln(R)$ on $T^{-0.5}$ for samples 1 – 3 in the cryogenic-to-room temperature range. (b) An I-V characteristic of sample 3, demonstrating ohmic behavior.
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FIG. 8. (Color online) (a) Dependence of $\text{Ln}(R)$ on $T^{-0.5}$ for samples 1 – 3 in the cryogenic-to-room temperature range. (b) An I-V characteristic of sample 3, demonstrating ohmic behavior.