Current-transport properties of $Ag-SiO_2$ and $Au-SiO_2$ composite films: observation of single-electron tunnelling and random telegraph signals

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Current-transport properties of Ag–SiO_2 and Au–SiO_2 composite films: observation of single-electron tunnelling and random telegraph signals

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Abstract. Current-transport properties of extremely thin composite films of Ag–SiO_2 and Au–SiO_2 (about 9 to 15 nm in thickness) were studied. The observation of the sample cross-section by high-resolution transmission electron microscopy revealed that only a few Ag (Au) nanocrystals exist across the films. In spite of the simple device structure (i.e. just sandwiching the granular film between Al electrodes) and very large electrodes (100 μm × 100 μm), Coulomb blockade (CB) and Coulomb staircase (CS) structures have been clearly observed at low temperatures. As the temperature rose, the CB and CS structures smeared out and random telegraph signals due probably to a charge trapped at the interfaces between the nanocrystals and SiO_2 matrices were observed.

1. Introduction

The current-transport properties of metal–insulator composite films have been the subject of intensive studies for a long time for both fundamental and practical reasons [1–6]. Composite films with a relatively low metal concentration consist of small metal particles dispersed in dielectric matrices, and are often called granular metal films. The conductivity (σ) of granular metal films generally exhibits a characteristic temperature (T) dependence expressed as $\ln(\sigma) \propto T^{-1/2}$ under low electric fields, independently of the kind of metal and insulator. Many theories [1–4] have been developed for deriving this relation. In these theories, the current transport was assumed to arise from the tunnelling of carriers between adjacent metal particles. An important factor taken into account in the theories is the electrostatic charging energy which is required to transfer an electron from one neutral particle to another. In some of the theories based on the critical path method [3, 4, 7], a granular metal film was modelled as a resistance network in which any site is connected by a finite tunnelling conductance to its nearest neighbour, and the macroscopic conductance of the whole system was assumed to be determined by a critical percolation conductance, which is the largest value of the conductance for which the conduction over a continuous path in the resistance network is possible. Although the theories were successful in explaining the observed $\ln(\sigma) \propto T^{-1/2}$ relation, the conduction mechanisms are not fully understood and the effects of the charging energy have not yet been observed explicitly.

The purpose of this work is to directly observe the effects of the charging energy on the transport properties of granular metal films. If the film is thin enough to contain only a few particles along the conduction path, single-electron tunnelling (SET) effects caused by

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the large charging energies of metal particles may be observable in current–voltage (I–V) characteristics as the Coulomb blockade (CB) and Coulomb staircase (CS) structures [8, 9]. However, detailed studies on such thin granular metal films have not been made so far, except for a local transport measurement using the tip of a scanning tunnelling microscope (STM) as one of the electrodes [6]. Information on the macroscopic conductance of very thin films is indispensable to fully understanding the conduction mechanism of granular metal films and proving the validity of the previous theories.

In this work, we have studied conduction properties of extremely thin granular Ag–SiO_2 and Au–SiO_2 films sandwiched between Al electrodes of size 100 μm × 100 μm. The plan and cross-sectional high-resolution transmission electron microscopic (HRTEM) images revealed that Ag or Au particles several nanometres in diameter (nanoparticles) are dispersed in the films. We will demonstrate that, in spite of the very large device size, such films exhibit clear CB and CS structures in the I–V characteristics. We will show that the observed step structures can be qualitatively explained by a semiclassical model of the Coulomb blockade [8, 9]. We will also report the observation of random telegraph signals (RTS) [10–12] due probably to single-electron traps at the interfaces between the nanoparticles and the SiO_2 matrix.

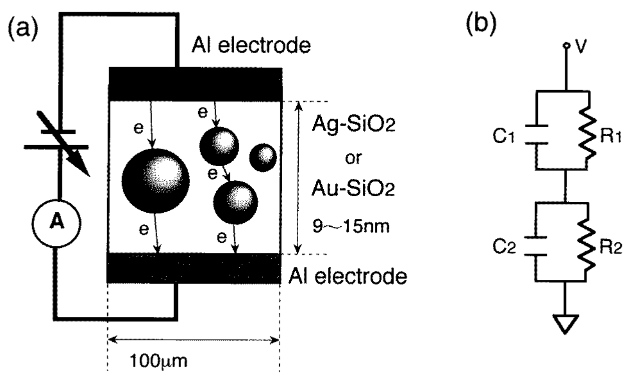


Figure 1. (a) The structure of the samples prepared, and (b) the equivalent electric circuit of the double-barrier tunnel junction model.

2. Experimental procedure

The structure of the sample prepared is quite simple, as is shown schematically in figure 1(a). An Al electrode 100 μm wide and 100 nm thick was first deposited onto a glass substrate. Granular Ag–SiO_2 and Au–SiO_2 films were then deposited by the cosputtering of SiO_2 and Ag or Au [13–15]. The volume fraction of Ag (Au) was controlled by varying the number of Ag (Au) chips placed on a SiO_2 target during the cosputtering. The thickness of the films was varied from 9 to 15 nm. The substrate was not intentionally heated during the cosputtering. After the cosputtering, an upper Al electrode (100 μm wide) was deposited. The upper electrode was arranged to make a right angle with the lower electrode. The active device area was thus 100 μm × 100 μm.

The dc I–V characteristics and the current as a function of time under constant bias voltage were measured by a Keithley 236 source measure unit in a temperature range from 2.5 to 300 K in an Oxford CF1204 continuous-flow He cryostat. After completing the measurements, the samples for the cross-sectional HRTEM observation were prepared by standard procedures including mechanical and Ar-ion thinning techniques. For plan-view HRTEM observations, the granular films were deposited onto KBr plates, wet stripped from the substrates and mounted on copper grids. The electron micrographs were taken by a JEOL JEM-2010 electron microscope operated at 200 kV.

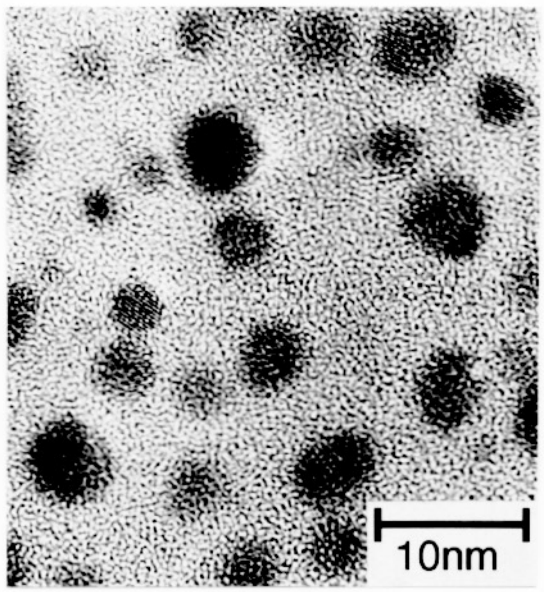


Figure 2. A high-resolution electron micrograph (plan view) obtained for a Ag–SiO_2 film. The volume fraction of Ag is about 1.5%. We can clearly see lattice fringes corresponding to the {111} planes of Ag particles with the fcc structure. The Ag particles are almost spherical and they are well dispersed in a SiO_2 matrix.

3. Results and discussion

3.1. HRTEM observation

Figure 2 shows a typical plan-view HRTEM image of a Ag–SiO_2 granular film (the volume fraction of Ag is about 1.5%). The dark patches seen are Ag particles embedded in a SiO_2 matrix. We can clearly see lattice fringes corresponding to {111} planes of the Ag particles with the fcc structure. The Ag particles are well dispersed in a SiO_2 matrix. The average size and the standard deviation obtained from the HRTEM images were 3.85 and 1.05 nm, respectively. Figure 3 shows a typical cross-sectional HRTEM image of the sample prepared under the same conditions as that shown in figure 2. The Ag–SiO_2 film is sandwiched between the two Al electrodes. We can see that Ag particles are randomly distributed between the two electrodes. Figure 3 suggests that current transport across the film occurs via Ag particles and that there exist many current paths between the two electrodes. Figure 3 also demonstrates that only a few Ag particles are contained in each current path. The HRTEM images obtained for Au–SiO_2 films were very similar to those of Ag–SiO_2 films.

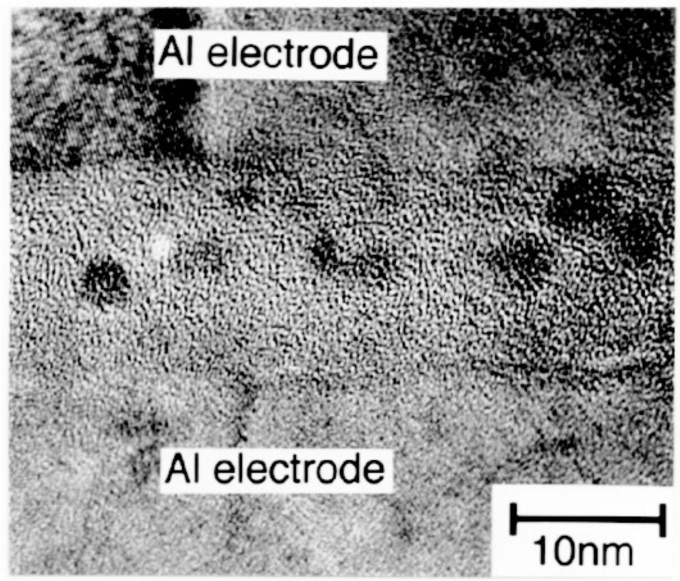


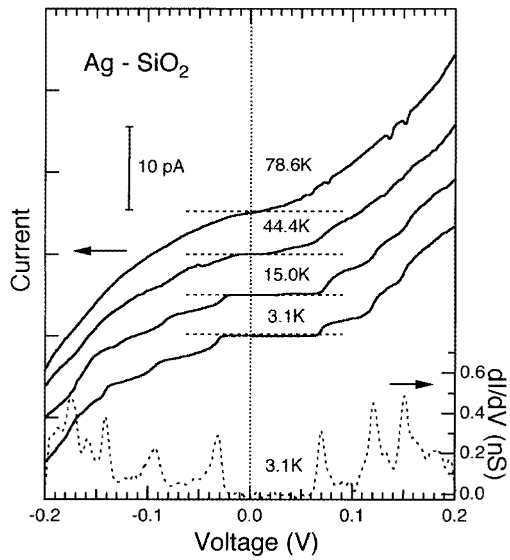
Figure 3. A cross-sectional high-resolution electron micrograph obtained for a Ag–SiO_2 film. The Ag–SiO_2 granular film is sandwiched between two Al electrodes. The dark patches seen are Ag particles in a SiO_2 matrix.

3.2. I–V characteristics

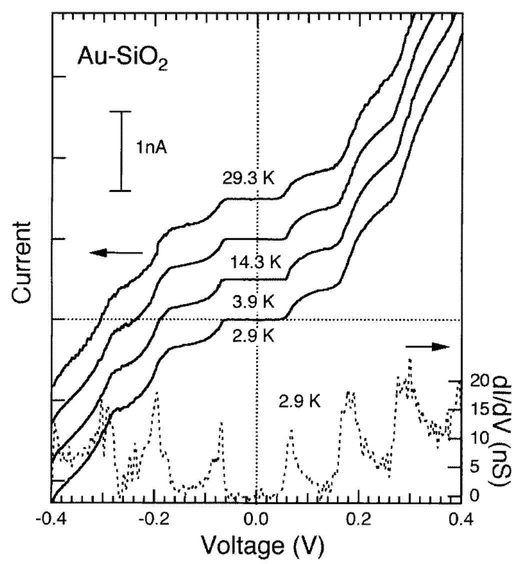
Figure 4(a) shows typical I–V characteristics of a Ag–SiO_2 granular film with a thickness of about 12 nm. At 78.6 K, we cannot see any distinct structures, except for the spike-like peaks at 0.075, 0.135 and 0.151 V. These peaks are not artefacts. We will discuss the origin of the peaks later. As the temperature decreases and reaches 44.4 K, step-like structures appear in the I–V curve, and the structure becomes clear as the temperature decreases. At 3.1 K we can see very clear step structures. The observed structures were quite stable. We measured the I–V curve by sweeping the bias voltage between −0.2 and 0.2 V many times. Although small changes in the step structures appeared, the period of the steps did not change during the measurement cycle, and no deterioration of the step structures was observed. Similar step-like I–V curves have been reported for the systems containing nanoparticles, and the observed step structures were assigned to the Coulomb blockade (CB) and Coulomb staircase (CS) structures [6, 16]. From the similarity of the I–V curves, we attribute the observed step structures to the CB and CS structures. This interpretation will be confirmed later.

The differential conductance curve obtained numerically from the I–V curve at 3.1 K is also shown in figure 4(a). We can clearly see sharp peaks. In this sample, the period of the peaks is not constant and the CB region is not symmetrical with respect to the zero bias. The CB region extends from −0.03 to 0.07 V. The width of the CS steps is distributed between 0.03 and 0.06 V.

In figure 4(b), the temperature dependence of the I–V curves and a corresponding differential conductance curve of a Au–SiO_2 granular film (9 nm in thickness) are shown. We can again see clear CB and CS structures. In contrast to figure 4(a), the differential conductance curve here is nearly symmetrical with respect to zero bias and the conduction peaks appear almost periodically. The period is about 0.125 V.



(a)



(b)

Figure 4. Temperature dependences of the I–V characteristics and a differential conductance numerically calculated from an I–V curve for (a) Ag–SiO$_2$ and (b) Au–SiO$_2$ granular films. Clear CB and CS structures are observed at low temperatures.

In this work, the CB structure in the zero-bias region was commonly observed for samples with different volume fractions of Ag and Au. However, only the samples with volume fractions of a few per cent exhibited clear CS structures. Furthermore, even for the samples prepared under nominally the same conditions, the observed step structures (step height, width and period) varied from one sample to another. Within the present work, we could not find any distinct difference between the I–V characteristics of Ag–SiO_2 and Au–SiO_2 films.

In the present samples, the current transport across the film is expected to occur via Ag or Au particles. Since the device size is very large (100 μm $\times$ 100 μm), a very large number of parallel local current paths are thought to exist between the two electrodes. In each current path, only a few metal particles are contained in it, as can be seen in the HRTEM image in figure 3. The local transport property of each path will be controlled by the charging energy of the particles contained in it, and the CB and CS structures will appear on the I–V curve of each local path. Such local transport properties of granular metal films can be studied by STM, and the observation of CB and CS structures has already been reported [6].

In contrast to the previous local transport measurements by STM, the I–V curves in this work may reflect the macroscopic conductance of the whole system. However, the observed I–V curves are very similar to those observed using STM [6]. It is very interesting to note that the present large devices with many parallel local current paths show clear CB and CS structures similar to those observed for a single path by STM.

If each local path in a large device has a similar conductance, the CB and CS structures observed for many paths will be smeared out by averaging the conductance of many paths. On the other hand, if the conductance of the local paths is distributed over many orders of magnitude, the macroscopic conductance of the films under low bias voltage is considered to be determined by a special path with the largest conductance. In this case, the CB and CS structures are expected to be observable even for a macroscopic-size device.

The successful observation of the clear CB and CS structures thus implies that the transport in the present sample is a highly selective process and that the charge moves along a special path with the largest conductance. The highly selective conduction properties may result from a large fluctuation of the local conductance due to the random distribution of the particle position and the size distribution. Since the local conductance of only one particular path is reflected in the macroscopic conductance of the whole system, a very small change in the sample structure will result in a drastic change in the conductance of the whole system. This may cause the observed strong sample dependence of the I–V curve.

In some of the theories predicting the $\ln(\sigma) \propto T^{-1/2}$ relation of granular metal films, the conductance of a whole system is assumed to be determined by just one preferential path with the critical percolation conductance [3, 4]. The present successful observation of the clear CB and CS structures for the very large devices seems to support the validity of the theories.

In the present samples, electrons are considered to be transferred via one, two or three particles along a path. If only one particle exists in the current path, the equivalent electric circuit is expressed as shown in figure 1(b) (the double-barrier tunnel junction model) within the semiclassical model of the CB [8, 9]. In this model, the number of excess electrons on a Ag particle is a periodic function of the applied voltage. This causes equidistantly spaced steps in the CS structure. The width of the steps corresponds to the charging voltage of a particle by a single electron (e/C), where C is the grain-to-environment capacitance. We found that the I–V curve in figure 4(b) can qualitatively be explained by the model, although the quantitative reproduction of the experimental curve was not possible. In the semiclassical model [8, 9], the tunnelling resistance is independent of the applied voltage, and the CS structure appears on a linear I–V curve. On the other hand, the observed CS structures appear on a nearly parabolic background. We believe that the deviation from the model is caused by the non-linear I–V characteristics of the thin SiO_2 tunnelling barriers. In fact, we observed non-linear I–V curves for extremely thin ($\leqslant$1 nm) SiO_2 films not containing metal particles. It should be noted here that the conductance of SiO_2 films not containing metal particles with the same thickness as that of the present Ag–SiO_2 and Au–SiO_2 films was too small to be measured by our measurement system (the minimum detectable current was about 10^{-13}A) for the temperature and bias voltage ranges studied.

Although the theoretical reproduction of the experimental curve was not possible, the capacitance could be estimated from the step width. The step width of 0.125 V for the sample in figure 4(b) corresponds to the capacitance of 1.3 aF. To confirm the above interpretation of the observed step structure, we will compare the capacitance with that estimated from the sample structure. Since the tunnelling resistance is very sensitive to the barrier width, the current path with the largest conductance is expected to contain a particle whose size is in the larger-side tail of the size distribution. The diameter of the largest particle that we found from HRTEM images is about 5 nm (the average size was about 2.9 nm). Taking the dielectric constant of the SiO_2 matrix as 3.9 and assuming that the distance between the Au particle and the Al electrode is 2 nm, the capacitance of the Au particle with respect to the Al electrode can be estimated to be 1.5 aF by the method of image charges [17]. Although the calculated capacitance differs a little from that estimated from the step width, the difference is sufficiently small to bear out the basic consistency of our interpretation.

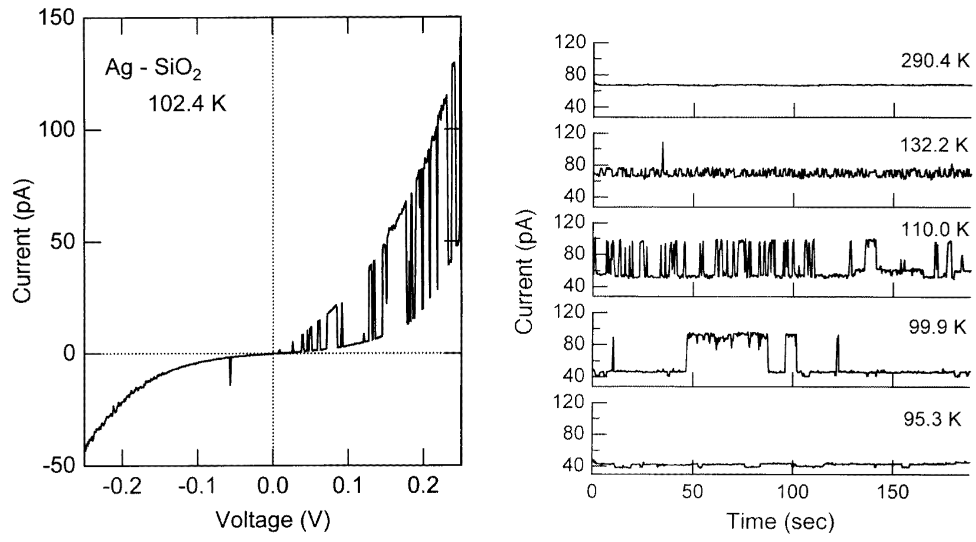
In contrast to the case for the sample in figure 4(b), the I–V curve of the sample shown in figure 4(a) could not be explained, even qualitatively, by the double-barrier tunnel junction model because of the non-periodic step width. It has been reported that three or more tunnel junctions arranged in series produce non-periodic I–V curves [6]. Since the maximum number of Ag particles arranged in a single path is about three as can be seen in figure 3, the dominant tunnelling path of the sample in figure 4(a) may contain two or three particles. We tried to fit the I–V curve assuming two or three particles in the current path. However, due also to the non-linear background of the I–V curve, reproduction of the experimental I–V curve was impossible. In figure 4(a), the I–V curves are not symmetrical with respect to zero bias. The asymmetries were often observed for the I–V curves of the systems containing nanoparticles and are considered to be due to a fractional electron charge on a particle [6, 8].

3.3. Random telegraph signals

In figure 4(a), the I–V curve observed at 78.6 K exhibits spike-like peaks at 0.075, 0.135 and 0.151 V. These peaks are not artefacts, and they are noises showing telegraph-like switching behaviour. We commonly observed these noises for the samples exhibiting CB. These noises were mainly observed at temperatures where CB and CS structures are almost smeared out (around 100 K) by thermal energy. Figure 5(a) shows a typical I–V curve at relatively high temperature (102.4 K) for a Ag–SiO_2 film. In this sample, the current switches between the two states and the switching occurs at a random interval under the positive bias. The amplitude of the step is very large and is larger than the lower current level. This type of noise is called random telegraph signals (RTS) [10–12].

Figure 5(b) shows the current as a function of time measured at various temperatures for a Ag–SiO_2 film. The bias voltage was set to 0.2 V. As the temperature increases the amplitude and the frequency of the switching first increase and then decrease. Although the RTS was commonly observed for the samples exhibiting CB, the number of states observed and the step amplitude varied between samples. Furthermore, the polarity of the voltage exhibiting the RTS also varied from one sample to another.

The RTS is considered to be caused by a capture or emission of a single electron at traps having energy levels within a few k_BT of the Fermi level. The observed very large



(a) (b)

Figure 5. (a) The I–V curve of a Ag–SiO_2 film measured at 102.4 K, and (b) current versus time for a Ag–SiO_2 film at five different temperatures. The bias voltage is 0.2 V.

step amplitude implies that the conductance of the films is substantially affected by the trapping of a single electron. This supports our previous conclusion that the conductance of the present samples is not an average of many paths, but is dominated by just one special path. Although we could not identify the origin of the trap within the present work, it is likely that the trap exists at the interface between a metal particle and a SiO_2 matrix.

4. Summary

We have succeeded in observing clear CB and CS structures as well as random telegraph signals for Ag–SiO_2 and Au–SiO_2 granular films with macroscopic-size (100 μm $\times$ 100 μm) electrodes. The observation of the CB and CS structures implies that the current transport in the Ag–SiO_2 (Au–SiO_2) granular films is made via Ag (Au) nanoparticles by tunnelling, and that the electrostatic charging energies of the particles play an important role in the transport properties of the granular metal films with relatively low metal concentration. Furthermore, the present results suggest that the transport in the granular metal film is a highly selective process, and that the transport is dominated by just one special path with the largest conductance.

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References

[1] Abeles B, Sheng P, Coutts M D and Arie Y 1975 *Adv. Phys.* **24** 407
[2] Abeles B 1976 *Applied Solid State Science (Advances in Material and Device Research 6)* (New York: Academic)
[3] Šimánek E 1981 *Solid State Commun.* **40** 1021
[4] Sheng P and Klafter J 1983 *Phys. Rev.* B **27** 2583
[5] Hohl G-F, Baranovskii S D, Becker J A, Hensel F, Quaiser S A and Reetz M T 1995 *J. Appl. Phys.* **78** 7130
[6] Bar-Sadeh E, Goldstein Y, Zhang C, Deng H and Abeles B 1994 *Phys. Rev.* B **15** 8961
[7] Ambegaokar V, Halperin B I and Langer J S 1971 *Phys. Rev.* B **4** 2612
[8] Hanna A E and Tinkham M 1991 *Phys. Rev.* B **43** 5919
[9] Grabert H and Devoret M 1992 *Single Charge Tunneling* (New York: Plenum)
[10] Kirton M J and Uren M J 1986 *Appl. Phys. Lett.* **48** 1270
[11] Smith R A and Ahmed H 1997 *J. Appl. Phys.* **81** 2699
[12] Sakamoto T and Nakamura K 1997 *Superlatt. Microstruct.* at press
[13] Hayashi S, Kato A and Yamamoto K 1994 *Solid State Commun.* **89** 563
[14] Fujii M, Nagareda T, Hayashi S and Yamamoto K 1991 *Phys. Rev.* B **44** 6243
[15] Fujii M, Nagareda T, Hayashi S and Yamamoto K 1992 *Japan. J. Appl. Phys.* **61** 754
[16] Andres R P, Bein T, Dorogi M, Feng S, Henderson J I, Kubiak C P, Mahoney W, Osifchin R G and Reifenberger R 1996 *Science* **272** 1323
[17] Stratton J 1941 *Electromagnetic Theory* (New York: McGraw-Hill)