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# Analysis of electrical and optical properties of silicon nanoclusters using flicker-noise spectroscopy†

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**This paper presents the results of a study on the electrical properties, chemical composition and photoluminescence from silicon nanocrystals produced by electrochemical etching of silicon wafers. A new phenomenological tool, known as flicker-noise spectroscopy (FNS), was used to analyze the experimental data. The electrical and optical signals from silicon nanoclusters are quite noisy. We show that FNS can be applied efficiently in analysis of these signals, allowing one to obtain significant information on the nature of dynamic microscopic processes assisting the flow of the electric current and emission of light from silicon clusters. The FNS method is also suitable for resolving the problem of the irreproducibility of the properties of nanostructured materials and devices. Deviations in size, local chemical impurities, structural defects and other micro-inhomogeneities strongly influence the output signals from nanostructures and make their characteristics poorly reproducible. The FNS approach makes it possible to scale the output information from nanostructured devices to a level where these deviations and irreproducibilities are no longer important. Copyright © 2001 John Wiley & Sons, Ltd.**

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## 1 INTRODUCTION

The process of electrochemical dissolution of monocrystalline silicon in hydrofluoric acid converts it into a highly porous matrix (known as porous silicon — PSi) with the pore walls containing tiny nanocrystals of silicon.[1]

PSi layers exhibit interesting non-linear optical and electrical properties,[2,3] making the material very attractive for practical applications in light-emitting devices, solar cells, sensors, etc. Still, there is much controversy in understanding the properties of PSi. For example, the well-known red luminescence of PSi is attributed to the radiative recombination of excitons in silicon nanocrystals, to luminescence from oxide substances, which passivate the nanocrystals, and to other physical effects.[4] The electrical conductivity of PSi layers is attributed to Schottky emission, hopping conductivity, and tunneling mechanisms, to mention but a few.[5]

An important problem in the physics of silicon nanocrystals that has not been the focus of research attention is that of noise. The optical and electrical signals originating from PSi are quite noisy. This noise has always been considered an undesirable artifact of the data acquisition and great efforts have been made to filter the noise out (smoothing, fast Fourier transform, etc.). We assume, however, that the noise is a source of useful information about the non-steady state phenomena occurring in nanocrystals as a result of energy impact (heating, illumination, application of electric field), or relaxation effects due to structural and chemical transformations in nanocrystals.

The presence of the noise in the information coming from a system of silicon nanocrystals is caused by a number of reasons. First, the overall quantity of material is small, and the sensitivity of analytical equipment becomes very important in acquiring the signals. This type of equipment-related noise will not be considered in this paper.

The other reason for the appearance of noise is the variation of physical properties of nanocrystals (their size, orientation, passivation, etc. can vary over a wide range). To reduce this factor one has to improve the reproducibility of the properties of nanoclusters, and this is quite a difficult practical problem. Finally, the noise can appear as a response of nanoparticles to the impact of energy (thermal, mechanical and electrical relaxation effects). In this case the noise is, in fact, a sort of information on the internal degrees of freedom in the system being studied.

It is important to understand how the noise is related to the properties of the nanoparticles to be able to extract useful information on their properties (micro-inhomogeneities of the structure, physical and chemical properties, etc.).

A variety of approaches developed have been to treat noisy signals. Non-linear time series analysis (TISEAN) is based on the analysis of the stochastic signals using a so-called autocorrelation function broad time series represented in a frequency domain.[6] Recently, a new tool has emerged, known as flicker-noise spectroscopy (FNS)[7], which expands the possibilities of existing methods by introducing a more complete set of characteristic functions.[7,8]

FNS allows one to subtract analytical information about the elementary processes taking place in complex physical systems from noisy signals. The application of the FNS method in the analysis of the electrical and optical characteristics of silicon nanocrytals is studied in this paper.

## 2 EXPERIMENTAL SET-UP AND BASIS OF THE FNS METHOD

### 2.1. Set-up for sample preparation, optical and electrical measurements

The electrochemical set-up used in the work to produce porous silicon layers has been described previously.[9] An AUTOLAB-30 potentiogalvanostat was used to control the current flowing through the electrochemical cell and to measure the voltage $V_a$ between the anode and a reference electrode. Both the counter-electrode and the reference electrode were made of platinum wire. The sample holder allowed a 5 $mm^2$ surface area of the silicon samples to be exposed to the electrolyte solution. We used p-Si samples (2–10 Ω cm) with orientations of (100) and (111). The backs of the samples covered with an Al–Si alloy to provide an ohmic contact.

The anodization process was conducted in the galvanostatic regime, where a constant current was forced to flow though the system and the anodic potential at the sample was registered as a function of time $V_a(t)$.

The electrolytes used in the work were 50% ethanoic solutions of 48% HF and 0.1 M $H_3PO_4$ + 0.001 M HF aqueous solution. The first electrolyte was used to form the porous silicon. The second electrolyte allowed for the observation of very regular and long-lasting oscillations of the anodic potential.[10]

Luminescence measurements were performed using an LS-50B spectrofluorimeter (Perkin Elmer) in the working range 400–900 nm with a spectral resolution of 0.5 nm. The temperature of the samples during the luminescence measurements was maintained in the range 11–450 K using a gas-flow helium cryostat (APD Cryogenics).

FT-IR analysis of the samples was performed using a System-200 spectrophotometer (Perkin Elmer) equipped with attenuated total reflectance (ATR) and diffuse reflectance (DR) accessories.

Finally, electrical characterization of the samples (d.c. and a.c. electrical conductivity measurements) was performed using the AUTOLAB-30 potentiogalvanostat as a polarization source. A mercury electrode contacted the top surface of the samples, and the contact to the back surface was obtained by pressing the sample against a polished gold electrode.

All experimental data obtained on PSi layers (beginning with the kinetic data on its growth and ending with optical spectra and electrical conductivity characteristics) are quite noisy. To ensure that the noise was not an artifact of the measurements (due to low sensitivity of the equipment used in the data acquisition), we performed control measurements of test samples using the same equipment and the same data acquisition modes. These samples were: for electrical measurements — high-stability electrical resistors RCA-1433; for optical measurements — GaAs laser diode.

### 2.2. Basis of FNS

The FNS method assumes a high information content of the sequences of non-regularities (bursts, jumps, discontinuities of derivatives) of any dynamic function $V(t)$ of variable $t$. This function can be a time series (e.g. the dependence of the anodic potential on the anodization time during PSi

 

formation), a topography map (i.e. roughness of surface films), and also energy spectra, when the independent variable is a wavelength or related parameter, and the function is an intensity of the spectral signal.

Two functions play an important role in the FNS method: (1) the power spectrum $S(f)$ of the autocorrelation function $\psi(\tau) = < V(t)V(t+\tau) >$ and (2) the structural function $\Phi_p(\tau)$ of order $p$, where $f$ is the effective 'frequency' and $\tau$ is the 'time shift' (these two parameters have dimensions of hertz and seconds for time series, and reciprocal nanometers and nanometers for optical spectral data, etc.).

A set of basic phenomenological parameters is introduced to serve as a fingerprint of the process studied. These parameters may be obtained by theoretical fitting of power spectra and structural functions calculated from the experimental data.

It has been shown[7,8] that the main contribution to the power spectra is produced by a sequence of bursts showing $V(t)$ dependence. Possible correlation links in the sequence of these non-regularities are calculated using the following interpolation formula:

$$S(f) \approx \frac{S(0)}{1 + (2\pi f T_0)^n} \qquad [1]$$

Here, $n$ is a parameter that characterizes the rate of 'memory' loss (correlation links) in the sequence of bursts within temporal intervals smaller than $T_0 \equiv (\lambda_0 K_0)^{-1}$. The lower the value of $n$, the longer is the memory. The parameters $n$, $T_0$ and $S(0)$ form the group of invariant basic parameters ('passport data') of the system under consideration. They characterize the degree of correlation in a sequence of the burst-like non-regularities of the signal. Their numerical values are obtained by fitting the experimental $S(f)$ dependencies using the Equation [1].

The dependencies $\Phi_p(\tau)$ are determined mainly by the 'steps' of the dynamic variable $V(t)$. The interpolation equation for the structural function of order $p$ is given by

$$\Phi_p(\tau) \approx g(p)\sigma^p[1 - \Gamma^{-1}(H)\Gamma(H, \tau/T_1)]^p \qquad [2]$$

where $\sigma$ is the dispersion of the dynamical variable $V(t)$, $H$ is the so-called Hurst constant, which characterizes the rate of memory loss in a sequence of step-like changes of dynamic variable, $T_1 = (\lambda_1 K_1)^{-1}$ is the characteristic interval of losing the memory (measured in time units for time series, in wavelength units for spectral series, etc.), $\Gamma(s)$ and $\Gamma(s, x)$ are the Gamma function and incomplete Gamma function. These are the basic constants complementary to those introduced by $S(f)$. They are derived from fitting the experimental data using Equation [2].

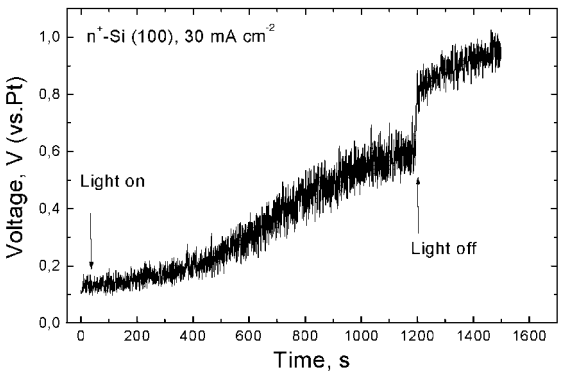


**Figure 1** Kinetics of PSi growth on highly doped n-Si (100) at 30 mA $cm^{-2}$ in the presence of light illumination (first 1200 s of polarization) and in the dark (final 300 s).

## 3 EXPERIMENTAL RESULTS

### 3.1. Kinetics of PSi growth

Typical polarization kinetic curves for the formation of PSi on n-Si wafers under UV light illumination and in the dark are presented in Figure 1.

As follows from Fig. 1, the $V_a(t)$ characteristics signals are quite noisy, which is generally a typical feature of aggressive corrosion processes.[11] We have demonstrated a very high sensitivity of the FNS method towards the analysis of the noise during the formation of PSi layers.[9] One of the remarkable features we have noticed is that the n-type and p-type silicon wafers show rather different $S(f)$ and $\Phi_p(\tau)$ characteristics (much higher dynamic memory for the n-Si case); this is obviously due to the differences in the mechanisms of the porous layers growth. Here we will expand the applications of the FNS method to examine the properties of PSi layers.

### 3.2. Photoluminescence (PL) from PSi layers

The PL spectra from PSi samples acquired at different temperatures and at an excitation wave-

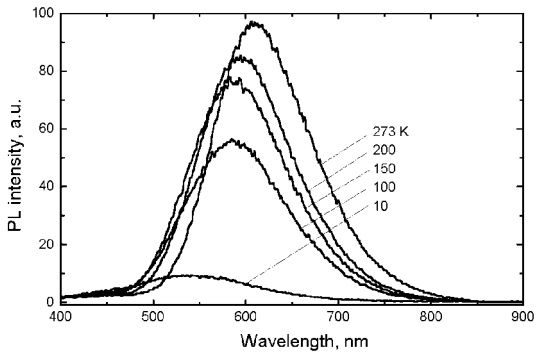


**Figure 2** PL spectra of PSi layers formed on $n^+$-Si registered at different temperatures using a 250 nm excitation wavelength.

length of 250 nm are shown in Fig. 2. One can see that the luminescence yield increases with temperature. The noise associated with the PL signal also increases, as is shown in Fig. 3.

Figure 4(a) demonstrates the power spectra of the noise presented in Fig. 3 and its fit using the FNS method. As follows from the analysis, the characteristic correlation interval for the PL spectra is rather small (1.2 nm at 10 K and 1.0 nm at 273 K). Values of the coefficient $n$ are excessively large (of

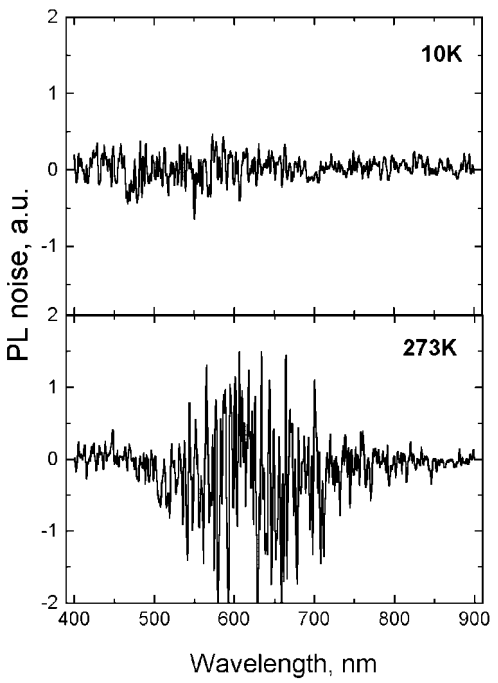


**Figure 3** Noise component corresponding to the PL spectra acquired at 10 k and 273 K. Note the differences in amplitude of noise and its spectral position.

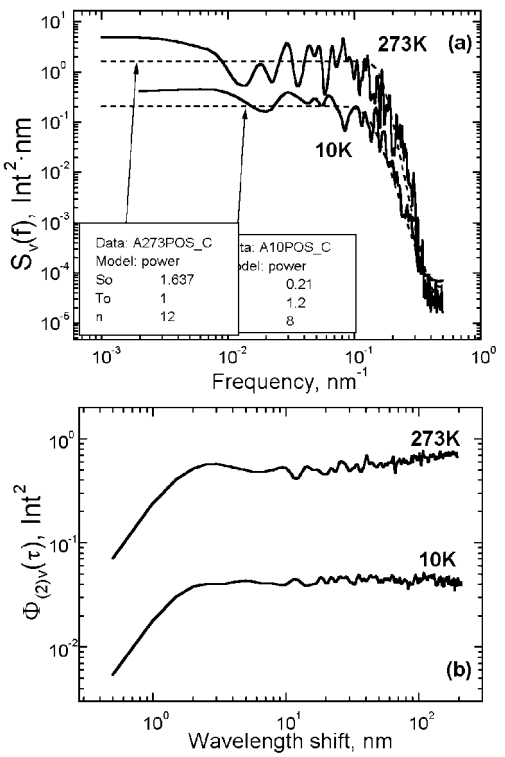


**Figure 4** Power spectra (a) and second-order structural functions (b) corresponding to the noisy signals shown in Fig. 3. The insets in (a) show the values of fit parameters ('Passport data' for PL spectra).

the order of ten), thus showing the rapid loss of the correlation links in a succession of individual events contributing to the PL spectra of PSi. This means that the energy states involved in the PL mechanism are quite weakly correlated with each other.

The absence of correlations is confirmed by the curves representing second-order structural functions (Fig. 4(b)). Though the saturation value for the curve representing the noise at 273 K is larger than that at 10 K, there is practically no dependence of $\Phi_2(\tau)$ on the wavelength shift, showing that the noise is close to what is called 'white noise', where no correlation links are present.

This weak (if any) correlation of luminescence events in PSi can be a factor to take into consideration in analyzing the mechanism of its PL (see Section 4). These are the very first results on the FNS analysis of the photoluminescence behavior of Si nanoparticles. Further work is necessary to to get convincing conclusions on the luminescence mechanism.

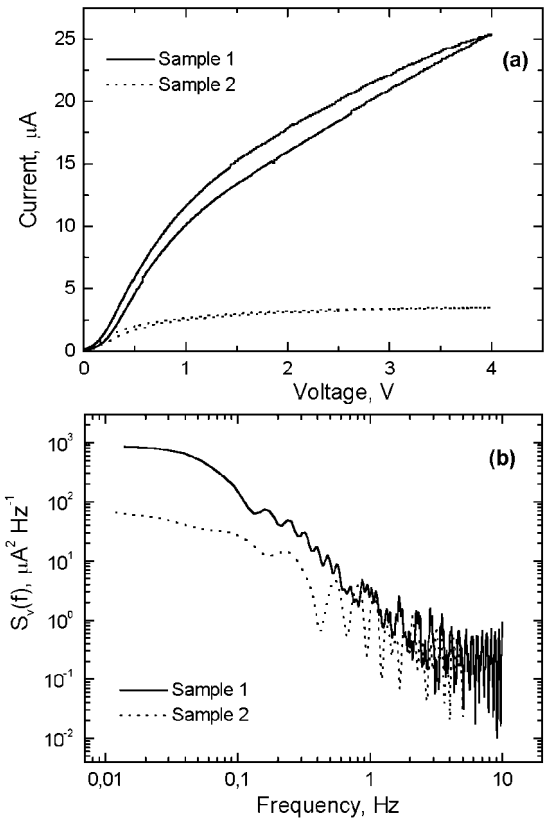


**Figure 5** *I–V* chracteristics taken at two different surface points of the thin (70 nm) PSi layer (a) and their representation using power spectra (b).

## 3.3. D.c. conductivity of PSi layers

Our previous paper[12] concentrated on the d.c. conductivity of thin porous silicon layers. We showed that the FNS method was suitable for studying the different relaxation effects in the d.c. conductivity of PSi associated with the structural relaxation processes.

Here we will concentrate on the applicability of the FNS method to studying the reproducibility of *I–V* curves obtained using different samples. Figure 5(a) illustrates the *I–V* characteristics of the PSi layers contacted with a mercury probe at different points on its surface. One can see that there is an essential scattering of the values of the current flowing through different sites on the sample surface due to a strong heterogeneity of the sample properties. Such irreproducibility, of course, is a negative feature that limits the application of PSi films in functional electronics (for example in sensors).

Figure 5(b) shows the power spectra for the *I–V* data. One can immediately notice that, unlike the original curves presented in Fig. 5(a), those processed using FNS are very similar.

# 4 DISCUSSION

First, we would like to discuss the observed absence of the correlation links in the spectra PL of PSi. These results show that there is no interaction between energy states involved in the radiative recombination mechanism. Let us imagine two neighboring silicon clusters, obviously different in their size and other physical properties. The UV excitation of one of them would obviously change the physical properties of the other (even the escape of the excited electron into the neighboring nanocrystal via a tunneling mechanism[4]). Thus, the interaction between silicon nanocrystals should cause some correlation links in the integral PL spectra, which is not the case here.

Therefore, we can conclude, though indirectly, that the FNS analysis presents some evidence of an alternative luminescence mechanism to that of excitons in silicon nanocrystals. In effect, if one considers the mechanism associated with surface passivation centers, which does not depend on the size and properties of silicon nanocrystals, then the input of different centers into the luminescence will be independent and statistically non-correlated.

These are the very first results on the FNS analysis of the PL behavior of silicon nanoparticles. They are to be expanded in further work to obtain convincing conclusions on the luminescence mechanism.

Another interesting issue to discuss here is the possibility of the application of the FNS method in processing poorly reproducible signals emitted by nanoparticles or devices fabricated on that basis. This problem is quite frequent in the operation of microminiaturized devices.

The results from FNS processing of the data on d.c. conductivity of different structures for PSi films (which are originally quite different from one another) show that the processed data are very similar to each other.

The same similarity effect is observed when PL spectra from PSi layers are compared. Their integral spectra can be very different, but after processing the PL data with FNS they yield very similar curves.

These observations open the possibility to use

FNS in processing the information from miniaturized devices. Though the integral yield can differ greatly due to possible irregularities of the properties of the structures, the FNS response is essentially the same, because this is due to microscopic processes taking place in nanoparticles, which are less sensitive to macro-inhomogeneities than the integral yield of the structures.

## 5 CONCLUSIONS

The application of FNS technology to the analysis of noise in electrical and optical signals allows the study of very fine differences in the kinetics of the formation of PSi layers, and their electrical and optical properties.

(1) We have found that while the processes of the formation of porous layers on n-type and p-type silicon are very different in their FNS characteristics, their optical properties are similar concerning the stochastic component of the luminescence signal.
(2) We observe very short correlation links in PL spectra (about 1 nm in wavelength scale). This might be interpreted in terms of a luminescence mechanism that is not related to the silicon clusters (where we should expect longer correlation links), but is rather due to species passivating these clusters (oxyhydride complexes).
(3) The FNS method is useful for increasing the reproducibility of the output signals from microminiaturized devices, as it allows one to scale the information down to a microscopic level where macro-nonuniformities of the signal no longer play a role.

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