Reaction-diffusion effects and spatiotemporal oscillations under SEM, STM and AFM-assisted charging in fiber-like and wire-like systems: From molecular and quantum wires to cooperative ferroelectric nanofibers and microfibers

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ABSTRACT: This review addresses the problem of reaction-diffusion effects and spatiotemporal oscillations in fiber-like and wire-like systems under the electron beam in SEM and in the presence of electric field in some special AFM techniques, such as current sensing atomic force microscopy (CS-AFM)/conductive atomic force microscopy (C-AFM), electrostatic force microscopy (EFM) and Kelvin probe force microscopy (KPFM) also known as surface potential microscopy. Some similar reaction-diffusion effects also can be observed in scanning capacitance microscopy (SCM), scanning gate microscopy (SGM), scanning voltage microscopy (SVM) and piezoresponse force microscopy (PFM). At the end of this paper the authors provide analysis of their own results and approaches. In particular, the possibility of achieving the ion transfer controlled growth of cells along the ion concentration gradients in reaction-diffusion fibers and actuators is indicated. This fundamental idea is discussed within the framework of the implantable fiber “bioiontronics” and “neuroiontronics” controlled by acoustic and electrical signals that regulate the reaction-diffusion or chemical oscillation activity of such fiber structures as reaction-diffusion actuators and sensors. The literature review includes more than 130 references.

KEYWORDS: dielectric charging; reaction-diffusion; iontronics; nanofibers and microfibers

1. Introduction

Effects of incremental charging of molecules and supramolecular structures under the tip of the scanning tunnelling microscope are well known since 1990s[1]. Such effects (taking into account Coulomb interaction of electrons) are the basis of the theory of quantum wire states[2]. Sablikov et al.[3], write that, “The chemical potential difference that exists between a decoupled, isolated quantum wire and the reservoirs gives rise to charge transfer in the coupled system… the quantum wire can be charged positively or negatively or remain neutral as a whole, depending on such factors as the wire radius and the background charge density in the wire. The magnitude of the charge and its sign are to a large extent determined by the exchange interaction of the electrons in the wire… The period of the oscillations depends on the charge acquired by the wire and the exchange energy[3].” Consequently, the effect of incremental charging of the quantum wires in various conditions can be interpreted as the

reaction-diffusion process with many possible oscillation regimes. Despite the fact that, “The linear conductance is… a function of the chemical potential”, the authors write, “The nonadiabatic transition from the reservoirs to the wire leads to conductance oscillations caused by multiple scattering of electron waves… and the exchange interaction strongly enhances the Friedel oscillations near the contacts.” The charging effect can be visualized not only at the repolarizable/resonant quantum wires with bistability (when “the system becomes unstable with respect to fluctuations of the electric potential and the electron density” and instabilities are the result of multistable electron states), but also in semiconductor quantum dot and wire arrays. Only the background of the surface physics for low-dimensional systems (for example—1D metallic segments at the quantum wire or 0D quantum dots) can be used for the description of charging and transport in the quantum or molecular wire systems, including very complex multiterminal and fractal-like branched ones. Models of such phenomena must be multiphysical, because they must consider all types of interactions (including non-covalent ones) and forces at the surfaces of quantum or molecular wires, which must be spatially colocalized with conduction maps. In the ideal case of a time-resolved (4D) approach in the analysis of charging of 1D systems the charge pattern must be colocalized with nanomechanics and mobility/motility of the wires” at the time-resolved (“time-lapse”) multilayer map for different forces and levels of energy/charging.

A crucial problem of the wire theory application in the past twenty years is its focusing only on the nanoscale phenomena and misuse of the terms “nano-” or “nanowire” in some situations, which blurs the meaning of the terms when they are inapplicable or beyond the technical level of the experiment. This terminological confusion blurs the distinctions between the real nanoscale wires, where quantum effects are observed, and microscale wires, where they can be neglected/ignored. However, from the precision Si nanosensors and single electron charging nanowire quantum dots to macroscopic lithium-ion batteries or supercapacitors, “charging nanowires” are widely used as a term. At the same time, it is quite obvious that “charging nanowires” in the case of supercapacitors and lithium-ion batteries can be replaced by “microwires” without changing the term meaning and physical sense of the effects observed. As it is known, the influence of quantum effects and the importance of “quantization” increases inversely with the nanowire diameter for a given material. When comparing different materials, the significance of quantization depends on their electronic properties, in particular on the effective mass of electrons. This means that the significance will depend on “how the conduction electrons interact with the atoms within the analyzed material”. In practice, semiconductors start to exhibit a clear effect of conductance quantization at sufficiently large transverse wire dimensions (100 nm), since their electronic levels already increase at such parameters due to the spatial restrictions. As a result, the Fermi wavelength of the electrons increases and splitting of the energy levels with sufficiently low energies occurs. This means that they can only occur at cryogenic (several K) temperatures, when the thermal excitation energy is lower than the energy of transitions between states. A quantum wire is just a conductive wire in which quantum effects influence the transport phenomena. Due to quantum restrictions on the conduction electrons in the transverse direction of wires, their transverse energy is quantized into a number of discrete values. In other cases, nanowires as well as supramolecular or molecular wires may not be considered as the quantum wires.

We proceed from the fact that it is difficult to work with single quantum wires and nanowires due to both physical and technical limitations. Therefore, we firstly do not consider oscillations and reaction-diffusion processes for nanowires, and secondly, we carry out modeling using rechargeable and repolarizable microwire-like polymer ferroelectrics. For the above reasons, we move from the methods of
tunneling microscopy to the SEM (scanning electron microscopy) methods in different specific operation modes, including YMD.

The local dielectric charging induced by the line scanning during SEM observation is a well known phenomenon, which can be simulated using simple mathematical/statistical physical approaches (including those approved by the standards of NIST (National Institute of Standards and Technology)). The electric charging of electron microscopic specimens has been actively studied from 1960s or 1970s. Initially, this effect was perceived only as an obstacle to obtaining high quality SEM images. “The elimination of charging artifacts in the scanning electron microscope” was the main aim of SEM-assisted sample charging investigations at the earliest years of SEM development. Such artifacts can be detected not only by the SEM image drift/defocusing induced by charging during observation, but also by the signals of X-ray analysis, particularly in ESEM and variable pressure scanning electron microscopes. According to Miller, “The effects of charging of uncoated, highly resistive samples of energy-dispersive X-ray spectra are examined. It is observed that as sample charging increases, the continuum background and characteristic peaks at higher X-ray energies diminish. Modelling of the continuum background has allowed this effect to be related to the development of a surface potential on the sample.” And, “This potential reduces the effective accelerating voltage of the electrons and results in a decreased overvoltage necessary for excitation of higher-energy X-rays. This artifact may lead to erroneous results in compositional analysis based on such charging-affected spectra.”

There are many methods for suppressing and elimination of the charging artifacts, such as random or pseudo-random scanning, vector scanning and Rayleigh contrast stretching method. There are also many approaches that uniquely identify and compensate the charging signal. However, such methods for identifying the charging signal without its suppression and compensation also have significant methodical value, since they allow to study only the sample charging signals without taking into account another basic components of the microscopic image signals. For correct interpretation of the identified microsample charging signal it is necessary to consider its physical mechanism rather than formally filtered, eliminated (by identification and subsequent matched filtering of the signal) images/signal features spaces.

It is well known that after the first observations of the surface charging using scanning electron microscopes (which can be interpreted as the starting point for the development of the stroboscopic electron microscopy at MSU by G. V. Spivak and the prerequisites for the EBIC/EMF technique development) the surface charging of different chemical compounds was proposed as a characterization method of their surfaces (since 1970s till now, from inorganic to polymeric samples). Therefore, for spatiotemporal charging analysis not only inorganic, but also polymeric samples can be investigated. Since they are dielectrics, insulators in a primitive representation, elements of physics of the charging dielectrics under the electron beam are applicable to them in a certain approximation.

Instead of analyzing the quantized charging of the quantum wires/nanowires, we will consider the analysis of charging of fibrous polymeric ferroelectric or piezoelectric composites. They clearly demonstrate the effects of the charge wandering, polarization/repolarization, as well as electromechanical dynamics under the electron beam. Many effects characteristic for the conductor-insulator composites, semiconducting and percolating samples can be observed on the developed surface of polymeric ferroelectrics and composites based on organic ferroelectric materials (compare with the study of Campbell et al. and Barkay et al.). Note that charging of ferroelectrics and piezoelectrics in SEMs (for example, TGS) has been studied since 1988 and (corresponding to their generation modes) a metastable surface-acoustic wave contrast observed in a scanning electron
microscope has been also described in 1988\textsuperscript{49}. Accordingly, using the analysis of histograms (and possibly their central moments) from the SEM charging images\textsuperscript{50}, one can perform mapping of the ferroelectric or piezoelectric properties of such complex polymeric samples. It can be implemented not only in the case of the negative charging, but also in the case of a positive charge\textsuperscript{51,52}, which can be colocalized not only with the electron concentrations but also with the proton concentration in polymeric ferroelectrics (such as proton conductivity of PVDF\textsuperscript{53–62}). Of particular interest is the case of charging under the electron beam, taking into account the plasma emerging under the action of the electron beam\textsuperscript{63}. Note that the effects observed in this case are multiphysical and are not reducible to the simpler machinery of the nanowire charging in collisionless plasma\textsuperscript{64}.

As for the study of polymer ferroelectrics for space applications\textsuperscript{65–76}, it should be noted that the processes similar to those during the polymer irradiation under an electron beam in a vacuum SEM chamber can also be observed in real outer space conditions when spacecrafts are bombarded with the particles (electrons, ions) of galactic and solar origin\textsuperscript{77,78}. Even more interesting phenomena requiring surface charge compensation (including electromechanical ones) occur when observing dielectric samples in ESEM\textsuperscript{79,80} and CryoEM (in particular, hydrocolloids or biological samples\textsuperscript{81}). The mechanisms underlying such phenomena of the sample surface charging can lead to the shift in the accuracy of X-ray spectral analysis and chemical element map quality deviation in variable pressure scanning electron microscopy\textsuperscript{82,83}. None of the methods of local (“topical”) controlling over the surface charging by other chemical agents or labels can be used in the case of position sensitive chemical mapping (since it can be the source of metrological artifacts itself)\textsuperscript{84}. Consequently, the charging effect metrology in SEM can be based not only on the physical signal changes\textsuperscript{85}, but also on the qualimetry of the shift of calibration curves or chemical distribution curves and spectra. A situation can often arise when hardware suppression of the parasitic charging signals does not lead to the improvement in chemical metrology, since there is no improvement in charging at the level of the samples and detectors that record its signals in the X-ray spectral range\textsuperscript{86}.

Both nanotechnologists and users of nanotechnology-related equipment have a question: Why SEM is the best tool to study the charging of fibers, wires, linear structures in comparison with tunneling microscopy and AFM? Indeed, some AFM methods have been used to analyze the local (“topical”) charging of nanostructured samples since the 1990s, despite the fact that most of such results are classified as artifacts\textsuperscript{87}. However, the geometric requirements for the linearity or planarity of the sample in this case are extremely important/obligate. The possibility of the single particle (or nanocrystal) studying or single molecule measurements is the “reverse side of the coin” for the impossibility of analyzing three-dimensional geometrically complex samples with a mesoscopically developed surface. It is possible to study/measure the charging of single semiconductor nanocrystals\textsuperscript{88,89}, inorganic 2D layers\textsuperscript{90,91}, self-assembled monolayers\textsuperscript{92,93} and nanolithography-level 2D polymeric surfaces\textsuperscript{94} (using special amplitude modulated techniques). It is possible to measure not only contact charging of bulk or 2D planar layer insulator surfaces\textsuperscript{95}, but also single particle electrostatic charging\textsuperscript{96}, single molecule charging by atomic force microscopes\textsuperscript{97,98}, including regular, periodic charging of individual molecules coupled to the motions of an atomic force microscopy tips\textsuperscript{99}. But it is impossible to measure dynamic electromechanical coupling in 3D oscillating and strictionable piezoelectric polymer microwire systems in 3D space by AFM. In AFM one can measure only single electron charging effects for nanosystems\textsuperscript{100–103}, but can not measure synchronous cooperative electron transfer or transport of the charge gradients along the complex fiber. This is also true for quantum wires, because the simplest quantum wires can be made from metallic carbon nanotubes, which can be investigated by AFMs. It is
well known that it is possible to create macroscopic quantum wires based on carbon nanotubes, since in complex carbon nanotube filaments there is no need for each individual fiber to pass along the entire length of the wire due to the quantum tunneling of electrons, which creates tunnel transition from strand to strand. At the same time, it is obvious that AFMs cannot be used for the synchronous analysis of charging or charge transfer in such complex structures, while electron microscopy methods can be used for these purposes (since 1950s when specimen charging for latex particles was registered by TEM electron microscopes[104]). SEM techniques can be used for the analysis of charging of macroscopic complex and cooperative fibers up to the micron- and decamicro-scale radius fibers (e.g., hair[105–107]) (while AFMs can analyze the hair charging only at nanoscales, and not in a complex and mutual dependence of the charging of different hair fibers on each other[108,109]). Consequently, SEM technique is more optimal for the analysis of cooperatively driven ferroelectric fibers then AFM. It is quite obvious that oscillations observed in such systems are oscillations in distributed systems, and the corresponding models of the dynamics of reaction-diffusion processes in such systems should be interpreted as the models of 3D (4D) processes in distributed systems with spatiotemporal reactions under the electron beam, which is a control agent for the wave or pulse propagation with different charges and polarities (as Turing activators and inhibitors in the classical approaches[110–121]).

Further presentation of the experimental data obtained on bioferroelectric PHB fibers will be based on the approaches and assumptions described above.

2. Results and prospects

Figures 1 and 2 show dielectric charging of ferroelectric polymer fibers taking into account the action of the electric double layer[122,123]. The discrete and pulsating kinetics of the charge wandering along the fiber is observed, which corresponds to the reaction-diffusion model with the wandering waves. In the case of ionic or proton conductivity, rather than the conventional charge wandering, this system can be considered as a quasi-chemical ion-exchange system[124]. The effects of ionic conduction can be of great importance for biomedical iontronics and the creation of active implants, which can be stimulated and perform ion exchange with the environment during conduction of biological autowaves and chemical oscillations (for example, in cardiomyocytes and neuronal fibers)[125–128]. Moreover, despite the apparent homogeneity of the fibers, in fact they can be microheterogeneous, which corresponds to a different surface distribution of the charge/electric double layer. As a result, the charge wave propagation will be inhomogeneous even over the single fiber surface. Examples of this phenomenon from our work[129] are shown in Figures 3–5.

Many of these waves are associated with acoustic and mechanical vibrations of the fibers induced by the electron beam. Therefore, it is possible to develop the principles of design of the reaction-diffusion and autowave fiber systems. In such systems (potential scaffolds taking into account their biophysical biocompatibility) it is possible to achieve the ion transfer and controlled growth of cells along the ion concentration gradients during ion transfer and ion exchange (ion conductivity, including proton conductivity). In other words, not only implantable acoustofluidics based on such filamentous microfluidic structures can be implemented in the future, but also implantable “bioiontronics” and “neuroiontronics” controlled by the acoustic and electrical signals that regulate the reaction-diffusion or chemical oscillation activity of such fiber structures as reaction-diffusion actuators and sensors[130–133].
Figure 1. Dynamic images of the electric double layer charge propagation under electron beam at 500x magnification.

It can be seen that the charge isoline positions change in time and the charge propagation occurs cyclically, but not periodically, and the charge often accumulates on the heterogeneities of the fiber structure which prevent its further propagation\cite{122}. 
Figure 2. Dynamic images of the electric double layer charge distribution and propagation under the electron beam at 1000x magnification.

Perturbation of the double layer charge often influences the local fiber micromorphology\cite{122}.

Figure 3. Singular branched fiber with traveling charge waves on the surface (YMD micrographs after Sobel-Feldman operator visualizing isopotential lines of the electron beam induced emission)\textsuperscript{[129]}.
Figure 4. Charging isolines (isopotential lines obtained by Sobel filter) colocalized with SEM maps\cite{129}.
Figure 5. Oscilloscopic sectioning visualization of the surface charge propagation process performed in YMD-compatible registration mode (Y-modulation and raster carrier wave).

It is the point effect on the acute angle (or “arris”) of the fiber sample[129].

Conflict of interest

The authors declare no conflict of interest.

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