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Application of transmission electron microscopy for the study of a functional nanoelement

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Using the focused ion beam probe method, cross-section sample of a single functional device of micron dimensions were cut out for STEM and TEM studies. The use of analytical methods of transmission electron microscopy made it possible to obtain accurate data on the geometric parameters of nanoscale functional devices, the phase and elemental composition of functional element material, as well as on the concentration of free electrons at the Fermi level in the nanoelement material.

Keywords: Scanning transmission electron microscopy (STEM), high-resolution transmission electron microscopy (HRTEM), NbN thin superconducting films, cryogenic inductance element, electron energy loss spectroscopy (EELS)).

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Introduction

Advancements in modern technology are inexorably associated with the development of new functional elements. Many of them are nanoscale, and this size is the factor shaping their unique properties. Arrays of nanoscale magnetic elements (patterned media for high-density data recording [1]; photonic crystals based on ordered arrays of quantum dots [2]; nanoscale semiconductor electronic elements and emerging cryogenic electronic elements [3]; optical single-photon detectors based on superconducting nanowires [4]; elements with Josephson junctions [5]; biological single-molecule sensors; and many other types of devices may serve as examples here.

These structures are distinguished by the range of element sizes and the topology of element positioning, which specifies the functional characteristics of devices. The atomic composition, geometric dimensions, and crystal structure are important parameters of elements. It is impossible to construct functional devices without controlling for consistency of these parameters of fabricated elements.

Transmission electron microscopy (TEM) is a versatile experimental technique for examination of the microstructure and the atomic composition of materials. It may be used both in the broad parallel beam mode (HRTEM), which allows one to study the atomic structure in high-resolution images, and in the focused beam mode (scanning transmission electron microscopy, STEM), which provides data from nanoscale microstructure elements with localization corresponding to the electron probe diameter (in the present case, ~ 0.14 nm) [6].

The focused ion beam (FIB) method needs to be used in order to cut a sample (thin lamella) directly from the examined nanoscale element of the microstructure. Classical techniques for preparation of thin lamellae for TEM studies in the form of cross sections of bulk samples have been developed both for traditional scanning microscopes, which utilize only an ion beam (Ga, He, and Kr ions are applied), and for more advanced modern setups with ion and electron beams used simultaneously [7]. Dual-beam systems provide an advantage in combining the following two key features enhancing the quality of TEM samples: the potential to monitor the transparency of a lamella in secondary electrons in real time (by scanning this lamella with a electron beam in the direction perpendicular to the direction of thinning) in the process of ion-beam finishing and the potential to deposit protective layers with the use of an electron beam only, thus minimizing the energy of deposited atoms after the interaction of gas precursor molecules with beam electrons. The techniques for sample processing with dual-beam systems have advanced so significantly in recent times that a method for lamella preparation in a new cutting geometry (not in the traditional transverse direction, but parallel to the surface) [8,9] was developed for, e.g., the study of minerals, such as rare meteorites from Mars [10]. The technique for preparation of TEM lamellae is used actively in studies of frozen biological objects [11].

Niobium nitride is a promising superconducting material that offers fine processibility, stability, and a high superconducting transition temperature (~ 16 K in a bulk sample). Analytical studies of the microstructure of niobium nitride films were performed by fabricating cross-section samples in a traditional way that involves gluing a stack of plates

together, sticking the stack into a metal tube, cutting a thin ring, mechanical polishing of the end faces, and subsequent thinning by a broad beam of Ar ions at the center to achieve transparency for electrons [12,13]. This traditional method for preparation of a cross section is suitable only for continuous films, since it is impossible to pinpoint where a thin region of the studied material transparent for electrons will be formed.

In the present study, the specifics of FIB preparation of cross-section samples for the examination of an individual microscale element are discussed. A nanoscale superconducting inductive element of cryogenic devices is used as an example to demonstrate the potential of examination of the material microstructure and composition by STEM, TEM, electron energy loss spectroscopy (EELS), and analysis of high-resolution images.

1. Experimental procedure

A nanoscale inductive element based on a superconducting nanowire, which is used in cryogenic circuits [3], was examined. A long superconducting nanowire and its intrinsic kinetic inductance, which depends on the wire width and is directly proportional to its length, is utilized in the design of this functional element. A nanowire was fabricated by electron lithography and subsequent plasma-chemical etching from a continuous NbN film with a thickness of 8 nm on an oxidized silicon substrate.

Cross-section samples for microstructure studies were obtained using the FIB method at a „Helios Nanolab 650“ setup. The energy of Ga ions was set to 30 keV at the preparatory cutting stage and to 2 keV at the final smoothing stage.

The microstructure of the functional inductive element $\sim 20 \times 20\,\mu$m in size was examined using a cross-section sample prepared by the FIB method (a lamella was cut from the center of the structure perpendicular to the nanowires in Fig. 1).

Various lithography techniques (electron, ion, X-ray, nanoimprint lithography, etc.), which make it possible to form an element of the needed geometry at the required position on a substrate, are commonly used to fabricate small-size functional elements. However, the uniqueness and small dimensions of the studied element preclude one from using standard techniques for preparation of cross sections from bulk samples (large-area films), since they do not provide an opportunity to accurately localize the formation of an electron-transparent region within the examined object. Therefore, it is necessary to use such methods for preparation of cross sections that offer precise positioning of the site where thin lamellae are cut directly from the small-size element under study.

Thus, a FIB setup, which allows one to visualize the surface structure in secondary electrons by scanning it with a focused electron beam while performing precision surface etching by a focused beam of gallium ions, is needed.

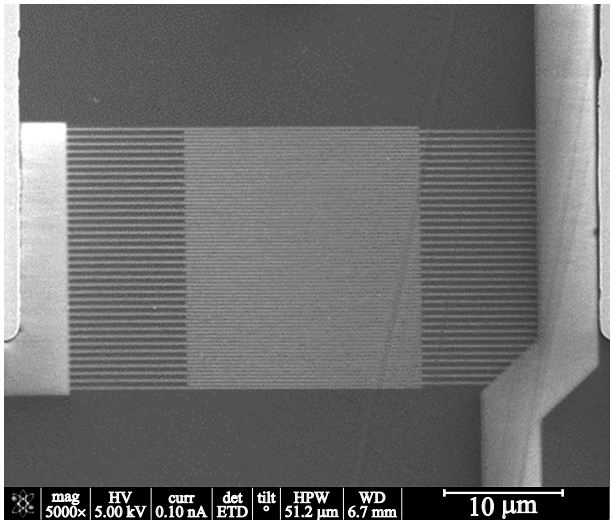

Figure 1. Inductive NbN element under study: long nanowire coiled into a meander to minimize the occupied area. Fine dielectric properties of the substrate after nanowire formation by etching of gaps provide an opportunity to visualize the ultrathin conductive nanowire with a scanning microscope (owing to a large difference in the secondary emission coefficient).

The deposition of protective layers onto a surface before cutting is an important stage of preparation of lamellae for examination of a nanostructured sample of a thin-film material. This protection is normally provided by a platinum layer that is deposited using a special organo-metallic gas, which decomposes under the influence of an electron beam. Although the deposition rate is low, it is imperative that an electron beam be used for deposition of the first protective layers directly onto the sample surface. An ion beam, which provides a higher deposition rate, may be applied only after the formation of this first protective layer. Effects of distortion of the microstructure and the composition of thin surface functional layers have been observed on multiple occasions when a protective layer was formed with an ion beam applied right from the start. This is attributable to the fact that a considerable energy is transferred to deposited metal atoms from a beam of 30 keV gallium ions.

A „Titan 80-300ST“ transmission electron microscope (the electron energy was 200 keV) and a „GIF-2003“ electron energy loss spectrometer were used in microstructure studies.

2. Results and discussion

Figure 2 shows dark-field images of the microstructure obtained in the scanning transmission mode. A protective platinum layer deposited in the process of FIB cutting of a lamella is seen at the top. A distinct z-contrast is apparent; bright regions are enriched with heavy elements (in the present case, niobium atoms). The mean nanowire width $(142 \pm 6\,\text{nm})$, the structure period $(212 \pm 8\,\text{nm})$,

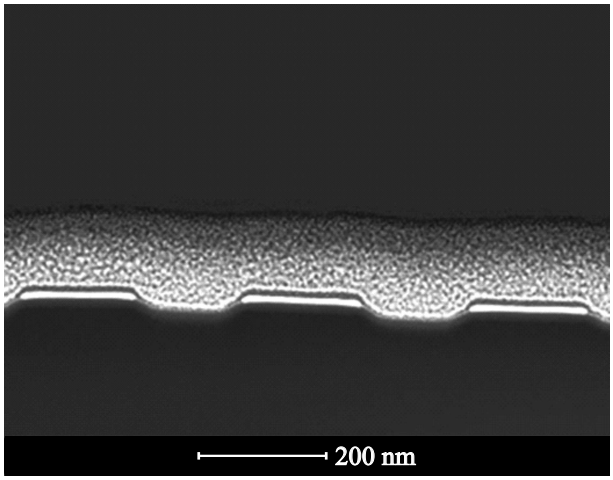

Figure 2. Cross section of the examined inductive element imaged in the dark-field high-angle scanning transmission mode. The dependence of the contrast on the atomic number of an element reveals the presence of heavy atoms (Nb) in the superconducting nanowire material.

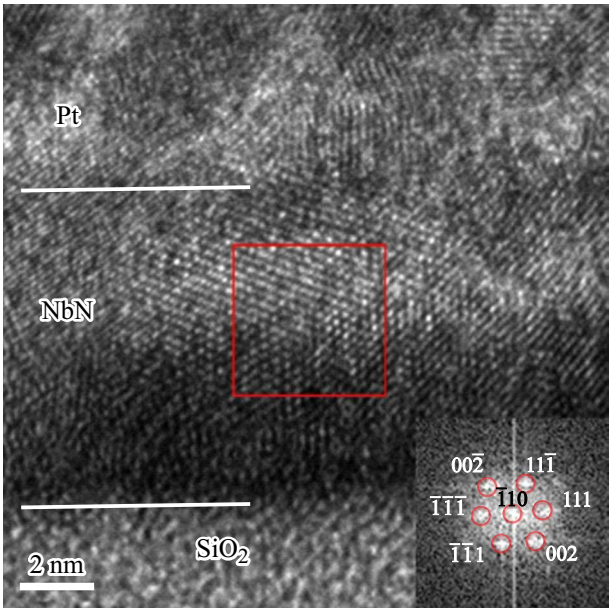

Figure 3. Atomic structure of the studied inductive element (cubic niobium nitride NbN) imaged in the transmission mode. Fourier transform pattern (inset).

and the characteristic spread of these parameters over a large number of nanowire sections (a lamella includes the sections of all nanowires forming the inductive element) were determined using a similar image with a greater magnification. Thus, STEM images provide an opportunity to measure accurately the geometric parameters of the inductive element that specify its characteristics.

High-resolution images of the nanowire material (Fig. 3) made it possible to determine the phase composition of its grains. The Fourier transform of the selected region (see Fig. 3) revealed elements of symmetry of the nanowire material structure that was found to belong to cubic system Fm-3m with a lattice constant of 0.439 nm, which corresponds to the NbN crystalline phase typical [14] of the used cathode sputtering method for deposition of a thin niobium nitride layer [15].

The results of elemental analysis of nanoscale grains, which was performed with the use of the method of relative atomic concentrations [6] by examining the characteristic electron energy loss spectra shown in Fig. 4, confirmed additionally the validity of identification of the phase composition of the superconducting polycrystalline material of the inductive element. Curves *1* and *2* in Fig. 4 represent the typical electron energy loss spectra with the background substracted for the $M_{4,5}$ niobium line and the K nitrogen line, respectively. The atomic concentrations of Nb (50 at.%) and N (50 at.%) in the material of the superconducting inductive element were determined by calculating the areas for Nb and N lines within spectral regions beyond the absorption edges with the corresponding cross sections of inelastic scattering processes [6] taken into account. The obtained values agree completely with the results of phase analysis of Fourier transform patterns for high-resolution images. Experimental measurements of atomic concentrations of elements are of vital importance as an additional confirmation of the validity of results of phase analysis, since this analysis just reveals the presence of certain elements of symmetry of the crystal under study and cannot be the sole argument in favor of identifying a specific known crystal phase (even if the calculated diffraction pattern of this crystal phase agrees well with the experimental Fourier transform pattern for a selected region of a high-resolution image).

Analytical scanning electron microscopy techniques involving the examination of electron energy loss spectra [16] provided an opportunity to determine the concentration of free electrons at the Fermi level in the nanowire material by

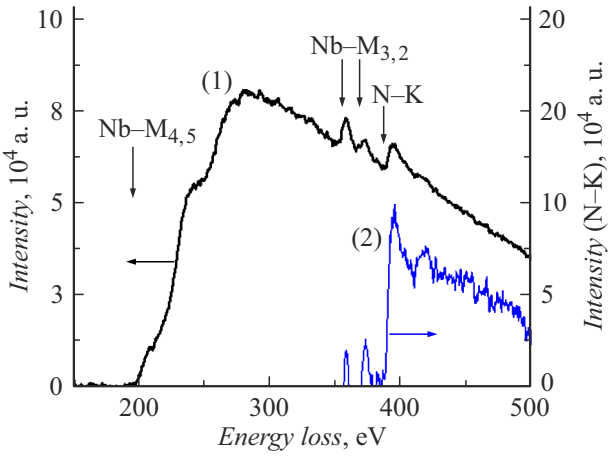

Figure 4. Characteristic electron energy loss spectra of the nanowire material with the background substracted: *1* — for the $M_{4,5}$ niobium line; *2* — for the K nitrogen line.

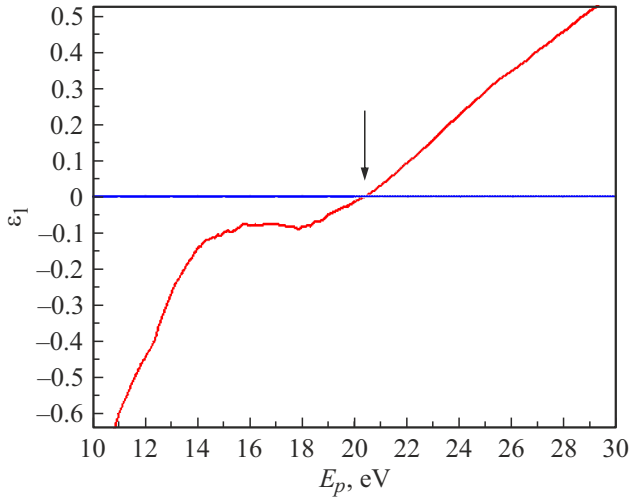

Figure 5. Energy dependence of polarizability ε_1 of the nanowire material.

analyzing the energy loss spectra in the region of excitation of plasmon oscillations.

Within the Drude model, concentration of free electrons n_e at the Fermi level is related to energy E_p of collective plasmon oscillations of electrons as

$$n_e = \varepsilon_0 m_e \left(\frac{E_p}{\hbar e}\right)^2, \qquad (1)$$

where $\hbar$ is the Planck constant, e is the electron charge, and m_e is the electron mass.

The initial energy loss spectrum is first subjected to deconvolution (to suppress the influence multiple scattering) and then undergoes the Kramers–Kronig transformation, which reveals the energy dependence of the real part of the complex dielectric response function of the electronic subsystem of the nanowire material ε_1 (polarizability) to an external excitation (see Fig. 5). Resonance peak E_p of the energy loss function corresponds to a near-zero E_1 value. Resonance energy E_p for NbN (indicated with an arrow in Fig. 5) assumes a value of 20.4 eV; the corresponding concentration of free electrons at the Fermi level calculated in accordance with formula (1) is $3 \cdot 10^{29}\,\mathrm{m}^{-3}$.

Conclusion

The scanning focused ion beam method and analytical TEM techniques were used successfully to characterize experimentally various parameters of an individual microscale nanostructured device (cryogenic inductive element in the form of a long nanowire fabricated from a thin niobium nitride film by common electron lithography and plasma-chemical etching). Geometric parameters of the cross section of a thin superconducting nanowire, the phase and elemental composition of the nanowire material, and the concentration of free electrons at the Fermi level (measured by analyzing the electron energy loss spectra in the region of excitation of plasmon oscillations) were determined by examining cross-section samples.

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Conflict of interest

The authors declare that they have no conflict of interest.

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