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Combined Scanning Nanoindentation and Tunneling Microscope Technique by Means of Semiconductive Diamond Berkovich Tip

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Abstract. A combined Scanning Probe Microscope (SPM) – nanoindentation instrument enables submicron resolution indentation tests and in-situ scanning of structure surfaces. A newly developed technique is based on the scanning tunneling microscopy (STM) with integrated Berkovich diamond semiconductive tip. Diamond tips for a combined SPM were obtained using the developed procedure including the synthesis of the semiconductive boron-doped diamond monocrystals by the temperature gradient method at high pressure – high temperature conditions and fabrication of the tips from these crystals considering their zonal structure. Separately grown semiconductive diamond single crystals were studied in order to find the best orientation of diamond crystals. Optimal scanning characteristics and experimental data errors were calculated by an analysis of the general functional dependence of the tunneling current from properties of the tip and specimen. Tests on the indentation and scanning of the gold film deposited on the silicon substrate employing the fabricated tips demonstrated their usability, acceptable resolution and sensitivity.

Introduction

The combined SPMs with diamond tips, also referred as Scanning Nanoindenters (SN) [1], scan the surface of materials and perform nanoindentation tests employing the same tip. Number of investigations was carried out in this field, for example, [2—4]. Kaneko и Oguchi [5] first proposed to utilize diamonds tips in combined STM. For the scratching and indentation experiments Hamada and Kaneko [6], Miyamoto [7,8], and Bhushan [9,10] used natural diamond tips sharpened as triangular pyramids with apex angles 60° and 80° and radius 100 nm. Some types of diamonds, particularly boron-doped, demonstrate good potential for the utilization as tips in conductive modes of SPM [5,11,12].

Existing examples of the application of semiconductive diamond tips obtained by chemical vapor deposition (CVD) in scanning probe microscopy give the proof of importance of such approach. However, CVD method usually requires the diamond annealing which can lead to its graphitization and degradation of working properties of tips. Besides, such diamonds demonstrate irregular structure.

Unlike CVD-diamonds, monocrystalline semiconductive diamonds have highly regular structure. Besides, distribution of the impurities in semiconductive monocrystalline diamonds has the zonal-sectorial structure. When employing the knowledge of the crystallographic directions, structure and local physical properties one can get the best balance of mechanical and physical properties.

SN commonly operates in surface force mode. Although our approach has limitation for non-conductive surfaces, the proposed combined SN-STM technique has two significant advantages. The first advantage is related to the high stiffness of tunneling probe. The second advantage of the instrument is its ability to obtain additional information, for example, to analyze each phase of nanocomposite surface separately.

1. Synthesis and selection of the semiconductive diamond crystals for tips fabrication

Diamond monocrystals synthesized from eutectic Mn0.54-Ni0.46-C0.1 alloy were obtained as an initial material for the fabrication of the tips for SPM probes [13]. Graphite type MGOSCh-7-3
containing not more than 0.007% of impurities has been chosen as a source of carbon. Powdered 99.9 at% pure boron with the grain size of about 10 µm was added in amount of 0.6 to 2.0 mas% as dopant to the load for diamonds’ synthesis. Synthesis was performed at the pressure of 4.0 to 4.2 GPa and temperature of 1260 to 1300 °C.

Most of synthesized crystals had octahedral or cubic habit, while twins appeared relatively rarely. Crystals are opaque and have dark color close to black. X-Ray crystallograms display well-identified $K_{a1,2}$ double on the last lines. This fact proves that the structure of highly boron-doped synthetic diamonds remains crystalline. Concentration of impurities has been determined my using µX-ray technique. When boron amount in the load grew from 0.6 mas% to 2.0 mas% acceptors’ concentration rose from $5.0 \times 10^{20}$ cm$^{-3}$ to $3.0 \times 10^{21}$ cm$^{-3}$ and ohmic resistivity of crystals changed from 50 Ω to 1.0 Ω at 300K.

Synthesized diamond crystals sized at around 0.5 mm were chosen to make tips.

![Fig. 1. Stages of processing of semiconductive diamond tip: (a) – synthesized semiconductive diamonds chosen for tips fabrication; (b) – determination of the cutting directions; (c) – zonal structure of the diamond crystal; (d) – Berkovich pyramid tip formation.](image)

Studies of the internal structure of crystals with different habits shown that crystals with octahedral habit have the most perfect built even when octahedral tips are dulled with {100} facets which form minor <100> growth pyramids. Crystals with preferentially developed octahedral facets (Fig. 1a) were chosen for the tips production. Such crystals have (as compared to crystals with other habits) higher conductivity because their volume is formed mainly by <111> growth pyramids providing higher conductivity due to the preferential absorption of boron dopant.

Diamond crystals chosen for tips manufacture had octahedral habit with clearly formed apexes and were inclusions-free.

Zonal structure of the crystal taken into account while grinding to obtain maximal conductivity in the apex of the tip is peculiar to our development of the probe tip’s fabrication technique (Fig. 1b). Thus cathode-luminescence study of the crystal was performed on the different stages of the grinding
for this purpose (Fig. 1c). While grinding, positioning of the tip’s working zone parallel to the <111> growth facet should be considered in order to achieve maximal conductivity.

Special cast-iron table subjected to the so-called “multi-year aging” was used as grinding tool. The working surface of the table has been impregnated with diamond micropowder with granularity less than 1 µm. Grinding parameters delivering standard required sharpness of the apex were determined.

REM image of the apex of semiconductive diamond tip is shown on Fig. 1d. The rounding radius of the apex was found to be about 80 nm.

2. Parameters of the tunneling between semiconductive diamond tip and the surface of specimen.

Specimen and tip were modeled as semiinfinite chains of the spherical potential wells with definite depths and radii. Wells’ depths correspond to the Fermi levels \( F_F \) for the tip and the surface. Scanning characteristics are \( V_t, I_t, d_t \), where \( V_t \) – tunneling voltage, \( I_t \) – tunneling current between tip and sample, \( d_t \) – tunneling distance. Wells’ radii \( R_{tip} \) correspond to the effective radius of tunneling channel.

Expression for the tunneling current valid for all values of the tunneling gap has been obtained:

\[
I_t = \frac{2e^2}{\hbar} V_t \left( \frac{\text{Im} \lambda_p \rho_p (d, E_F)}{D(\lambda_p, G_p)} + \frac{\text{Im} \lambda_s \rho_s (d, E_F)}{D(\lambda_s, G_s)} \right),
\]

where: \( d \) – tunneling gap, \( \lambda_s, \lambda_p \) – electron waves reflection coefficients from surface and probe correspondingly, \( D(\lambda_s, G_s), D(\lambda_p, G_p) \) – renormalizing local electron state densities denominators, required to take into account the effect of interelectrode electron waves reflections. \( \hbar \) – Plank’s constant, \( m \) – mass of electron, \( e \) – electron’s charge and \( V \) – tunneling voltage.

![Fig. 2. Theoretical dependences of the tunneling current vs. distance between the semiconductive diamond tip and the surface of the gold film for different applied voltages.](image)

Problem of determination of the tunneling current as a function of the distance between tip and a specimen’s surface, scanning characteristics, tip’s material and radius was solved using the fitting procedure [14] for the general wave function in the interaction area. Independence of the tunneling current from the polarity of the tunneling voltage \( V_t \) when \( V_t \ll 1\text{V} \) as approximating simplification was used to find the solution [15].

For small tunneling voltages and tunneling gaps conductivity of the tunneling zone has an extremum \( \sigma_{extr} = \sigma_{max} = 2e^2/\hbar \). In practice, however, in most cases extremal value of conductivity is less than the maximal value, i.e., \( \sigma_{extr} < \sigma_{max} \). Presence of the maximum of conductivity of the tunneling zone can be physically explained by the phenomena of the tunneling electron wave reflection from the tip and surface.
Fig. 2 shows calculation results derived from formula (1) for the gold film – diamond tip system. Hence nanometer resolution for 2 to 3 V tunneling voltage and submicron resolution for 0.5 to 1.0 V come out. Obtained dependences can be used to control SPM feedback system.

3. Experimental study.
Experiments had the purpose to test the fabricated tip for the combined surface studies which include tip’s indentation into the surface as well as its scanning.
Modified by authors STM made in Moscow State Institute of Electronic Technology used for experiments had the following principal specifications: Berkovich tip, horizontal and vertical resolutions better than 0.1 nm.

Gold films electrochemically deposited on the silicon substrate have been used as test specimens. Each experiment had three stages. During the first stage the specimen’s surface topography was obtained with scanning. On this stage instrument operates as traditional tunneling microscope. This stage ends up with the selection of the surface fragment for indentation and the tip’s shift to the center of the chosen fragment. Indentation is performed on the next stage. Obtained indent is scanned on the final stage.
Penetration of the tip into the specimen was determined by the control voltage applied to the Z-piezopositioner. To perform detailed study of the indentation parameters we tried to obtain indent large enough to fit the entire scanned frame on the gold film specimen with size up to 4×4 µm. Figs. 3a, c show 3D STM image of the indent together with its cross-section and profile after the indentation with maximal (250 V) Z-positioning control voltage. Since in the given experiment we have experienced cut-off of the bottom part of indent due to the limited film thickness, next experiment was performed with the control voltage of 150 V. In that case indent’s profile followed the probe’s profile (Figs. 3b, d).

4. Discussion
This paper represents one of the stages of the development of ISO-14577-compliant technique for mechanical testing of materials. The purpose of the current work was to implement two procedures of indentation and surface scanning employing the same probe. Practice of nanoprobe fabrication confirms that boron-doped 0.5 mm monocrystalline diamonds is a good material to manufacture Berkovich pyramid-shaped STM tips. Tip formed under proposed technology obtained regularly formed 80 nm apexes.
Availability of these tips enables micromechanical surface studies including nanoindentation, nanoscraping, and nanomachining of the state-of-the-art and future micromaterials, coatings and nanostructures. To implement all the potential of such instrument, a series of obstacles should be overcome. For example, as seen on the indents images the determination of the exact geometrical characteristics of the indents’ projections remains problematic. Specific pile-ups around indents are particularly noticeable. These formations generate significant difficulties for the development of the precise hardness measurement methods. We plan to investigate this phenomenon thoroughly in our ongoing studies of nanoindentation.

Conclusion
For the tips manufacture purposes semiconductive diamonds sized at around 0.5 mm with octahedral habit were selected considering their machineability requirements.

The fabrication technique has been developed that permits to produce Berkovich pyramid-shaped nanoprobe with ~80 nm apex. Quantum-mechanical modeling of the electron tunneling modes has been performed for the surface scanning using the semiconductive diamond tip. Experimental studies of the gold-plated specimens employing the developed tip and STM method have been carried out. These studies demonstrated the developed tip’s capability to perform complex nanoscale surface investigations combining indentation with the surface scanning.

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