Magnetoelectric effect in a sandwich structure of gallium arsenide–nickel–tin–nickel

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Abstract. The results of investigation of the magnetoelectric effect in a nickel-tin-nickel sandwich structure obtained by galvanic deposition of gallium arsenide on a substrate are presented. The technology of constructing such structures is described and the experimental results of the frequency dependence of the effect are presented. It is shown that the use of tin as an intermediate layer reduces the mechanical stresses resulting from the incommensurability of the phases, which permits obtaining qualitative structures with the nickel thickness of about 70 µm. The resulting structures exhibit good adhesion between the layers and have a high quality factor.

1. Introduction

The magnetoelectric (ME) effect, discovered more than half a century ago, recently attracts more attention of the researchers which is shown by an increasing number of publications on this subject [1]. This is due to the fact that rather many materials with the effect magnitude sufficient for practical applications have recently been discovered. This permits creating various devices of solid-state electronics such as magnetic field sensors or memory cells on the basis of the ME effect, which, by their parameters, are not only inferior but, in some cases, superior to the traditional devices. The composite materials consisting of magnetostrictive and piezoelectric phases are widely used to create such devices. These materials can be divided into two classes, bulk and layered. The bulk composites are manufactured by the ceramic technology and represent mechanically coupled mixtures of powders of magnetostrictive and piezoelectric phases [2, 3]. The layered composites consist of mechanically coupled magnetostrictive and piezoelectric layers [4–6], where the layers can be arranged both in parallel and in series. The structures can be shaped as plates, disks or rings with radial polarization and as cylinders. Both bulk and layered composites have their advantages and disadvantages. The bulk composite materials obtained by sintering the mixtures of ferrite and piezoelectric powders are easily manufactured and have good mechanical properties, but they have smaller ME parameters compared to the layered composites. The advantages of layered structures is a high degree of the piezoelectric phase polarization and small leakage currents, since the magnetostrictive phase with higher conductivity is isolated by the piezoelectric phase with high resistivity. In this case, the metals with a large magnetostriction coefficient can be used as a magnetostrictive
phase. However, great disadvantages of layered structures are the poor mechanical strength, stratification of the samples along the phase boundaries, and a low quality factor. Most of the layered structures are obtained using an intermediate polymer layer (glue) which degrades the parameters and leads to undesirably high temperature dependence and a decrease in the quality factor of the structure. In [7], the ME effect was studied in the structures where the magnetostrictive phase was applied to a piezoelectric substrate by the deposition method. This provides a good mechanical contact between the phases, but does not allow obtaining a large value of the effect. As was shown in [8], the maximum value of the effect is obtained under the condition $p_t\sqrt{p_Y} = m_t\sqrt{m_Y}$, where $p_Y$, $m_Y$ are the Young’s moduli of the piezoelectric and the magnet, respectively, and $p_t$, $m_t$ are the thicknesses. Young’s moduli of a piezoelectric and a magnetic material, as a rule, differ at most by two times, so the maximum value of the effect is obtained for approximately equal thicknesses of the magnet and piezoelectric. The use of the method of electrolytic deposition makes permits obtaining magnetostrictive layers whose thickness is commensurable with the thickness of the piezoelectric substrate. However, this raises the problem of adhesion. The better adhesion between the magnetostrictive and piezoelectric phases can be obtained by using pre-sprayed sublayers. As was shown in [9], the use of Au–Ge–Ni sublayers deposited on a GaAs substrate with subsequent electrolytic deposition of Ni allows obtaining structures with good adhesion between the layers. However, mechanical stresses arise due to the disparity of the lattice parameters, which, at large layer thicknesses, lead to distortion and destruction of the structure. In this paper, we propose a method for eliminating these stresses by creating a sandwich structure in which the electrolytically deposited layer of nickel alternates with an electrolytically deposited layer of tin.

2. Technique for manufacturing the structure

The initial samples were cut from plates with surface orientation (100) as parallelepipeds of dimensions $14 \times 4 \times 0.4$ mm so that their long side coincided with the $<110>$ direction of the crystal. In the production of layered structures, as a rule, the piezoelectric material is a material with the highest piezoelectric modulus value $d$. However, the calculations show [10] that the ME effect is directly proportional to the piezoelectric modulus and is inversely proportional to the dielectric constant of the piezoelectric material. Although the piezoelectric modulus of GaAs is 37 times smaller than that of a PZT ($d = -2.69$ pC/m for GaAs and $d = 100$ pC/m for PZT), its dielectric constant is 135 times smaller than that of a PZT ($\varepsilon = 12.9$ for GaAs and $\varepsilon = 1750$ for PZT). This implies that, under the other equal conditions, it is expected that the magnitude of the ME effect in GaAs based structures is almost the same as in the structures based on the PZT. However, unlike the PZT, gallium arsenide is a single crystal with more stable properties. It should not be preliminarily polarized and, in addition, a well-tuned semiconductor technology can be used in the production of structures.

To improve the adhesion to the samples, Au–Ge–Ni sublayers were previously deposited. Before plating, all samples were first contacted with a 0.2 mm diameter nickel wire or with a clamp. The samples were then degreased with Vienn lime or lambomide solution 203. Vienna lime is a mixture of calcium oxide and magnesium oxide. Degreasing with Viennese lime is done in small-scale production by hand using a brush. Thin slurry of Viennese lime is rubbed by brush onto the surface of the product, and then the product is washed with water. These operations were performed three times until the surface of the product was completely wetted with water. More efficient, less laborious, and allowing one to obtain high quality degreasing is the operation with the help of lambomide 203. For this purpose, a solution of lambomide 203 concentration from 30 to 40 g/l was used, and the solution was heated to 70–80°C. The degreasing time was 10–20 minutes. After degreasing, the samples were washed in hot water at a temperature of 60–80°C for 1 minute.

Electrolytic deposition of nickel generates high internal stresses and it is impossible to obtain
Figure 1. Coating installation 1 — anodes, 2 — heat insulation, 3 — device for mixing, 4 — contact thermometer, 5 — cathode, 6 — DC source, 7 — tubular electric heater, 8 — thermostat, 9 — water, 10 — electrolyte.

Table 1. Composition of electrolytes used to create the structures.

| Components of electrolyte | Electrolyte No. 1, g/l | Electrolyte No. 2, g/l |
|---------------------------|------------------------|------------------------|
| Nickel sulfate heptahydrate | 250                    | —                      |
| Nickel chloride hexahydrate | 50                     | —                      |
| Tin sulfate               | —                      | 60                     |
| Boric acid                | 25                     | —                      |
| Sulfuric acid             | —                      | 105                    |
| Preparation OS-20         | —                      | 4.5                    |

The total thickness of the multilayer structure was 157 μm. The coating on the gallium arsenide turned out to be smooth, frosted and without visible defects.
3. Magnetoelectric effect

The magnetoelectric (ME) effect in the structure was studied by measuring the voltage on a sample placed in a constant (magnetizing) and an alternating magnetic field (figure 2).

First, the field dependence of the low-frequency ME signal was investigated. At a constant value of the strength of the alternating magnetic field of 1 Oe, the dependence of the ME coefficient on the strength of the bias field was measured. Then, with the magnetization field strength corresponding to the maximum of the effect, the frequency dependence of the magnetoelectric coefficient in the electromechanical resonance region was investigated. The measurements were carried out when the permanent and alternating magnetic fields were directed along the long side of the sample. The singularity of the ME effect, when gallium arsenide is used as a piezoelectric, is that the nonzero components of the piezoelectric tensor are $d_{14} = d_{25} = d_{36}$, and therefore, the electric voltage induced on the sample plates arises due to shear deformations rather than to tension-compression deformations as in PZT. In our case, an alternating magnetic field directed along the long side of the sample (the Z axis) induces tension-compression strains in the magnetic component whose tensor, in the coordinate system associated with the sample, will be denoted by $S_{zz}$. These deformations are transferred to a piezoelectric which, as a result of piezoelectric effect, induced by the electric field. The equation of motion for the z projection of the displacement vector of the medium can be written as

$$\bar{\rho} \frac{\partial^2 u}{\partial t^2} = \frac{\partial T_{zz}}{\partial z}, \quad (1)$$

where $\bar{\rho}$ is the average value of the density of the sample, and $T_{zz}$ is the average value of the stress tensor of the sample.

The equations for the component of the strain tensors $pS_{zz}$ and the x projection of the electric induction $pD_x$ of the polarized piezoelectric phase take the form

$$pS_{zz} = \frac{1}{pY} pT_{zz} + p d_{x,zz} pE_x, \quad (2)$$

$$pD_x = p\varepsilon_{xx} pE_x + p d_{x,zz} pT_{zz}, \quad (3)$$

where $pT_{zz}$ is the component of the stress tensor in the piezoelectric phase, $pY$ is the Young’s modulus along the direction <011> (Z axis), $p d_{x,zz}$ is the piezoelectric tensor in the coordinate system.
system XYZ (see figure 2), $p_\varepsilon_{xx}$ is the dielectric tensor, and $pE_x$ is the $x$ component of the electric field.

The components of the piezoelectric tensor $pd_{x,zz}$ in the coordinate system XYZ connect with the components of the piezoelectric tensor $pd_{x,\beta}$ in a coordinate system associated with crystallographic axes by the following relation

$$d_{x,zz} = d_{14}\beta_{2}\beta_{3},$$  \hspace{1cm} (4)

where $\beta_{2z}$ and $\beta_{4z}$ are the cosines of the angle between the axes $Z$ and the axes 2 and 3 (the $<010>$ and $<001>$ directions).

Equations for the magnetostrictive phase can be written in the form

$$mS_{zz} = \frac{1}{mY} mT_{zz} + m_{q_{zz}} mH_z,$$  \hspace{1cm} (5)

where $mT_{zz}$ is the component of the stress tensor in the magnetostrictive phase, $mY$ is the Young modulus, $m_{q_{zz}}$ is the longitudinal piezomagnetic coefficient, and $mH_z$ is the magnetic field.

Let us represent the solution of the equation for the displacement vector of the medium in the following form:

$$u(z) = A \cos(kz) + B \sin(kz),$$  \hspace{1cm} (6)

where $A$ and $B$ are the integration constants.

Using the Eq. (6), we obtain the equation for the dependence of the frequency on the wave vector at the propagation of elastic waves in the magnetostrictive-piezoelectric multilayer structure in the following form

$$\omega = \sqrt{\frac{Y}{\rho}}k = \sqrt{\frac{mY^m t + lY^l t + pY^p t}{m\rho^m t + l\rho^l t + p\rho^p t}}k.$$  \hspace{1cm} (7)

4. Magnetoelastic voltage coefficient

The magnetoelastic voltage coefficient is defined as the ratio of the electric field $E$ induced by the magnetic field to the magnetic field $H$; i.e.,

$$\alpha_E = \frac{E}{H}.$$  \hspace{1cm} (8)

However, in contrast to bulk composites, the magnetoelastic voltage coefficient of layered magnetostrictive-piezoelectric structures can be defined in two ways. The first one is the ratio of the electric field induced in the piezoelectric to the magnetic field in the magnet producing this electric field; i.e.,

$$p\alpha_E = \frac{pE}{mH}.$$  \hspace{1cm} (9)

The magnetoelastic coefficient defined in this way characterizes well the efficiency of the magnetoelastic field transformation, i.e., the transformation of the magnetic field in the magnet into the electric field in the piezoelectric. However, under this definition, the magnetoelastic coefficient characterizes rather poorly the efficiency of the magnetoelastic transformation of the entire structure. In the experimental determination of the magnetoelastic coefficient, the voltage that appears across the capacitor plates is measured. The magnetoelastic coefficient defined by Eq. (9) is the higher the thinner is the piezoelectric layer, although in this case the voltage induced across the plates decreases. The second way of defining the magnetoelastic
voltage coefficient is the ratio of the average electric field in the structure to the magnetic field; i.e.,
\[ \langle \alpha_E \rangle = \frac{\langle E \rangle}{H}, \]  
(10)
where \( \langle E \rangle = U/(m^t + l^t + p^t) \) is the average value of the electric field in the structure and \( U \) is the voltage induced between the electrodes. The magnetoelectric voltage coefficient defined in this way quantifies the efficiency of the magnetoelectric transformation of the entire structure.

To derive the theoretical expression for the magnetoelectric voltage coefficient we use the method elaborated in our previous works [2–4]. First, the integration constants \( A \) and \( B \) entering Eq. (6) for the displacement vector of the medium are determined from the boundary conditions at the sidewalls of the sample. Next, the found values are substituted into Eq. (2) for the strain tensor of the piezoelectric, from which the component \( pT_{zz} \) of the stress tensor is expressed. Finally, found expression is substituted into Eq. (3) for the electric induction and the electric field in the piezoelectric and the magnetoelectric voltage coefficient are determined from the condition of an open circuit.

The conditions of mechanical equilibrium at the free sidewalls of the sample yield the following boundary conditions
\[ \int_0^{\Delta} pT_{zz}(\pm \frac{1}{2}L, x) \, dx + \int_{\Delta}^{l^t} pT_{zz}(\pm \frac{1}{2}L, x) \, dx + \int_{l^t}^{m^t} mT_{zz}(\pm \frac{1}{2}L, x) \, dx = 0. \]  
(11)
Using these boundary conditions, we find the expressions for the integration constants
\[ A = 0, \quad B = \frac{my^m \nu z_{zz} \langle mH_z \rangle + py^p p^n d_{zz,zz} \langle pE_x \rangle}{k \cos \kappa \left( m^t m^t Y + l^t l^t Y + p^t p^t Y \right)}, \]  
(12)
where we have introduced the dimensionless parameter \( \kappa = kL/2 \).

Having expressed the component of the stress tensor in terms of the components of the strain tensor from Eq. (2) and substituting the resulting expression into the equation for the normal component of the electric induction vector, we come to the equation of the form
\[ pD_z = p\varepsilon_{xx} pE_x + py^p p^n d_{zz,zz} \frac{\partial p u_z}{\partial z} - py^p p^2 (p d_{zz,zz})^2 pE_x. \]  
(13)
The electric field \( \langle pE_x \rangle \) induced in the piezoelectric is found from Eq. (10) with the use of the open-circuit condition \( I = 0 \). Taking into account this condition and the expression for \( B \) we find from Eq. (12) the following equation
\[ \langle pE_x \rangle = \frac{py^p p^n d_{zz,zz} p\varepsilon_{xx} \langle mH_z \rangle - \Delta \left( m^t m^t Y + l^t l^t Y + p^t p^t Y \right) \tan \kappa}{m^t m^t Y + l^t l^t Y + p^t p^t Y} \frac{m^t m^t \tan \kappa}{\kappa}, \]  
(14)
\[ \Delta = 1 - \frac{k^2}{p} \left( m^t m^t Y + l^t l^t Y + p^t p^t Y \right) \tan \kappa / \kappa. \]  
(15)
We will use the definition of the magnetoelectric coefficient given by Eq. (10) taking into account the fact that the voltage induced between the electrodes is \( U = \langle pE_x \rangle p^t \). Thus, we finally find the magnetoelectric voltage coefficient
\[ \alpha_E = \frac{py^p p^n d_{zz,zz} p\varepsilon_{xx} \langle mH_z \rangle - \Delta \left( m^t m^t Y + l^t l^t Y + p^t p^t Y \right) \tan \kappa}{m^t m^t Y + l^t l^t Y + p^t p^t Y} \frac{m^t m^t \tan \kappa}{\kappa}. \]  
(16)
According to Eq. (16), the frequency dependence of the magnetoelectric voltage coefficient is of the resonance type.
Figure 3. Frequency dependence of the sandwich structure of gallium arsenide-nickel-tin-nickel. The bias field is $H_{\text{bias}} = 360$ Oe.

Figure 4. Frequency dependence of the effect in the resonance region.

The experimental measurements of the frequency dependence of the structure are illustrated in figure 3.

As can be seen from the figure, the frequency dependence has a sharp resonance character. The ME value of the voltage coefficient is much lower than that in the pure structure of nickel-gallium arsenide [9], which is explained by the presence of a passive tin buffer layer. However, this structure has a very high quality factor. The frequency dependence of the effect in the resonance region is shown in figure 4.

As follows from the figure, the quality factor of the system is $Q = 800$, which is much better than the quality factor of the samples obtained by the gluing method and is comparable with the quality factor of bulk composites [3].
Conclusions
The use of an intermediate tin layer in the electrolytic deposition of nickel on an arsenide-gallium substrate permits obtaining structures with the nickel layer of thickness up to 70 µm. These structures have good adhesion between layers, good mechanical strength, high quality factor and are very promising for creating devices based on the magnetoelectric effect.

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