Surface contribution to the generation of reflected second-harmonic light for centrosymmetric semiconductors

O. A. Aktsipetrov, I. M. Baranova, and Yu. A. Il'inskiĭ

Moscow State University

(Submitted 3 February 1986)
Zh. Eksp. Teor. Fiz. **91**, 287–297 (July 1986)

We present a systematic analysis of the intensity anisotropy of reflected second-harmonic (SH) radiation for centrosymmetric crystals of the classes $m3m$ and 432. We discuss the possibility of separating out a contribution to the nonlinear-optical signal from a transition layer near the surface; this contribution arises from the loss of inversion symmetry. We also investigate the question of the uniqueness of such a separation. This surface contribution is investigated for the first time for the cleavage plane of germanium. We investigate the polarization selection rules for the process of reflection-induced SH generation. The connection between breaking of the selection rules and the surface topography is investigated experimentally for silicon. A remote nonlinear-optic signal method is suggested for monitoring micro-inhomogeneities at the surface of semiconductors and metals.

INTRODUCTION

In the last decade, optical methods for investigating solid surfaces have undergone significant developement. Application of modulation techniques, which increase the sensitivity of the recording system, along with the detection of giant amplification of optical phenomenon, have made it possible to study spectroscopically the surfaces of solids in single crystals, rather than in the finely-dispersed state. Along with the issue of sensitivity, the problem of principle importance with using optical methods is how to separate out the surface contribution (where by the "surface" we mean a thin layer containing several periods of the crystal lattice) from the total volume of the solid which is interacting with the light, i.e., a layer of thickness $\sim\alpha^{-1}$ where α is the absorption coefficient. This problem is rather easily solved for the case of giant Raman scattering of light (GRS)[1] and for second-harmonic generation by reflection from Langmuir films.[2] In these cases, a monlayer of molecules forms on the surface, whose properties differ significantly from those of the substrate; these differences allow us to distinguish the surface and volume optical responses.

The nonlinear-optic electroreflectance method developed recently makes it possible to isolate the SH signal at the surface of metals[3] and semiconductors[4] as a result of modulation of the nonlinear properties of the surface by a constant electric field. However, this method is most convenient for studying the boundary between a semiconductor (metal) and an electrolyte, since it requires application of a field with an intensity $\sim 10^7$ V/cm; it is difficult to create such fields under other conditions.

In the general case of an arbitrary medium, experimental identification of the optical signal from the surface is almost impossible; however, in some special cases this can indeed be done. In Ref. 5 we find mentioned for the first time the possibility that for centrosymmetric semiconductors of the class $m3m$, by virtue of the specific symmetry requirements, the SH signal generated by the near-surface layers on the (111) face can be separated out. This possibility is related to the fact that in centrosymmetric crystals, SH generation in dipole approximation is forbidden, and the volume contribution to the reflected SH connected with the quadrupole effects is very small. However, in a layer near the surface whose thickness is several periods of the crystal lattice, the inversion center is absent. This layer possesses a dipole quadratic susceptibility, and despite its small thickness can give rise to SH comparable to the intensity of the volume quadrupolar SH generated by a layer of thickness $\sim\alpha^{-1}$. The systematic analysis presented below (which is absent from Ref. 5) of the symmetry properties of the anisotropic nonlinear polarization in crystals belonging to the classes $m3m$ and 432 shows that for the (111) surface the nonlinear polarization contains both contributions: a dipolar surface and a quadrupolar volume contribution, while for a (100) [or (001)] plane only the volume contribution is present. This property of the quadratic polarization also allows us, by comparing the reflected SH signals for these two planes, to determine the surface contribution. Experimentally, the surface contribution can be isolated for a cleaved surface[6,7]; we will use the cleavage method in this paper for single-crystal germanium.

GENERATION OF REFLECTED ANISOTROPIC SH IN CRYSTALS OF CLASSES $m3m$ AND 432

In centrosymmetric crystals, the volume quadratic polarization $\mathbf{P}(2\omega)$ is different from zero only in the quadratic approximation, taking into account spatial dispersion, and is determined by the expression[8]

$$P_i^Q(2\omega)=\chi_{ijkl}^Q E_j(\omega)\nabla_k E_l(\omega), \tag{1}$$

where χ_{ijkl}^Q is the quadrupole correction tensor to the quadratic susceptibility, $E_j(\omega)$ are the components of the pump field, and ∇_k are the components of the operator ∇. For a plane wave, expression (1) takes the form

$$P_i^Q(2\omega)=\chi_{ijkl}^Q E_j(\omega)k_k E_l(\omega), \tag{2}$$

 0038-5646/86/070167-07$04.00

where k_k are the components of the wave vector of the pump within the nonlinear medium.

In the layer near the surface, there is no center of inversion, which leads to the appearance in this layer of a dipole quadratic polarization

$$P_i^D(2\omega)=\chi_{ijk}^D E_j(\omega)E_k(\omega), \tag{3}$$

where χ_{ijk}^D is the nonlinear susceptibility tensor in the interior of the layer near the surface. Since the thickness of the noncentrosymmetric layer d is small and comparable to the crystal period, we can introduce the concept of a surface polarization

$$P_i^S(2\omega)=\lim_{d\to 0} P_i^D(2\omega)d$$

and a surface susceptibility tensor

$$\chi_{ijk}^S=\lim_{d\to 0}\chi_{ijk}^D d. \tag{4}$$

In Fig. 1 we show the geometry of the region near the boundary under discussion. A plane pump wave with frequency ω falls on the surface of a nonlinear crystal at an angle ϑ_0 to the normal from the linear-medium side. Since our investigation is essentially connected with the crystal of the layer near the surface, we will consider the reflecting surface to be oriented parallel either to the (111) or (001) planes. The vector $\mathbf{E}_0(\omega)$ for the incident wave makes an angle ψ_0 with the plane of incidence (i.e., the polarization is arbitrary).

Let us choose a laboratory coordinate system x_0,y_0,z_0 in which the measurement of the intensity of the anisotropic SH $I^{2\omega}(\varphi)$ is carried out so as to make the boundary between the media coincide with the $z_0=0$ plane, and the

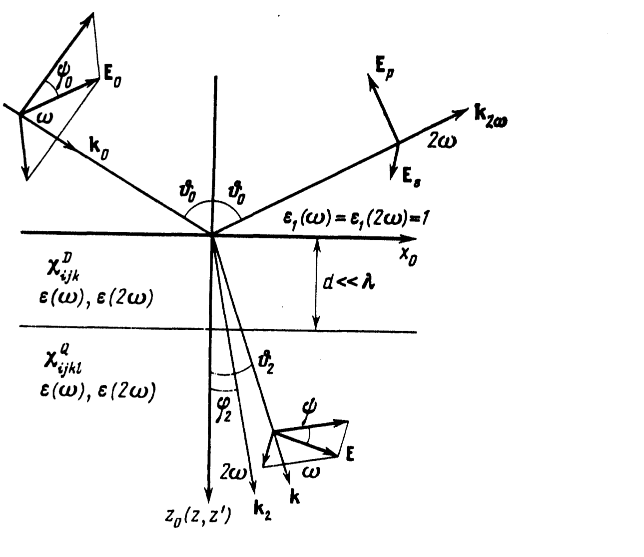

FIG. 1. Geometry for the interaction of light waves in the generation of SH by a semiinfinite centrosymmetric medium: $z<0$ is the linear medium, $z>0$ is the nonlinear medium; $0<z<d$ is the noncentrosymmetric transition layer near the surface; $z>d$ is the centrosymmetric volume; ϑ_0,ϑ_2 are the angles between the normal to the boundary and the wave vectors for the pump radiation k_0 and k in the linear and nonlinear media respectiely; φ_2 is the angle between the normal and the wave vector k_2 of the SH radiation in the nonlinear medium; E_0, E are the pump fields in the linear and nonlinear media respectively; ψ_0, ψ are angles between the plane of incidence and the vectors E_0 and E.

incident plane coincide with $y_0=0$; the nonlinear medium occupies the half-space $z_0\geqslant 0$. The angle φ determines the rotation of the crystal relative to the laboratory system of coordinates. The layer near the surface where the inversion symmetry is broken occupies the region $0<z_0<d$. For crystals of the $m3m$ class, the dielectric permittivity ε is isotropic; we will assume that it is the same in both the volume and the surface of the crystal. The latter assumption is a crude one, as is the introduction of a surface susceptibility (4); however, it has very little effect on the correctness of the final qualitative conclusions, which in essence are based only on symmetry considerations.

Along with the laboratory system, we introduce two other systems of coordinates which are closely tied to the crystal and rotated relative to the laboratory system. In the crystallographic coordinate system xyz, the reflection plane $z=0$ coincides with the (001) crystal plane. In the coordinate system $x'y'z'$ the reflection plane $z'=0$ is the (111) crystal plane, and the axes x' and y' are directed along the crystallographic directions $[2\bar{1}\bar{1}]$ and $[0\bar{1}\bar{1}]$. The axes z_0, z and z' of all three coordinate systems coincide. The rotation of the crystal in the laboratory system is defined by the angle φ between the x_0 axis and the x and x' axes.

To analyze the anistropy in the intensity of the reflected SH $I^{2\omega}(\varphi)$, it is necessary to know the forms of the tensors $\chi^S_{i'j'k'}$ and χ^S_{ijk} for the quadratic susceptibilities of the near-surface layers on the planes (111) and (001), and the quadrupole susceptibility χ^Q_{ijkl} of the class $m3m$ crystal. To determine the nonzero independent components of these tensors, it is convenient to make use of the method of "complex" coordinates, described, e.g., in Ref. 9, which allows us to take into account the symmetry elements of the point group of the object under discussion with ease.

In the crystallographic coordinate system the tensor χ^Q_{ijkl} from a class $m3m$ crystal takes the form

$$\begin{gathered}
\chi^Q_{xxxx}=\chi^Q_{yyyy}=\chi^Q_{zzzz},\\
\chi^Q_{xxyy}=\chi^Q_{xyyx}=\chi^Q_{yxxy}=\chi^Q_{yyxx}=\chi^Q_{xzzx}=\chi^Q_{xxzz}=\chi^Q_{yyzz}=\chi^Q_{yzzy}=\chi^Q_{zxxz}\\
=\chi^Q_{zzxx}=\chi^Q_{zyyz}=\chi^Q_{zzyy};\\
\chi^Q_{xyxy}=\chi^Q_{yxyx}=\chi^Q_{xzxz}=\chi^Q_{yzyz}=\chi^Q_{zxzx}=\chi^Q_{zyzy}.
\end{gathered}\tag{5}$$

The near-surface layer in the (001) planar possesses symmetry $4m$, and in the crystallographic coordinate system the tensor has the form

$$\begin{gathered}
\chi^S_{zzz},\\
\chi^S_{xzx}=\chi^S_{xxz}=\chi^S_{yzy}=\chi^S_{yyz}.
\end{gathered}\tag{6}$$

For the (111) plane, things become more complicated. The face itself, i.e., the outermost monolayer of atoms, has symmetry $6mm$ (Fig. 2).[10] This centrosymmetric two-dimensional structure contributes no anisotropy to the nonlinear polarization.[11] However, the loss of inversion symmetry refers to several atomic layers beneath the surface; taking its loss into account lowers the symmetry of the layer near the surface on the (111) plane to $3m$.[10] In this case, the tensor $\chi^S_{i'j'k'}$ in the coordinate system $x'y'z'$ takes the form

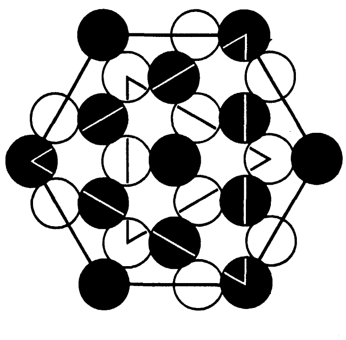

FIG. 2. Top view of the (111) plane of a class $m3m$ crystal: ● is the first atomic layer, ○ the second. The symmetries of a monolayer with this structure belong to the point group $6mm$. A threefold axis and m-plane are common symmetry elements for two (or a larger number of) such layers (point group $3m$).

$$
\begin{gathered}
\chi^{S}_{z'z'z'},\\
\chi^{S}_{x'x'x'}=-\chi^{S}_{x'y'y'}=-\chi^{S}_{y'x'y'}=-\chi^{S}_{y'y'x'},\\
\chi^{S}_{x'z'x'}=\chi^{S}_{x'x'z'}=\chi^{S}_{y'z'y'}=\chi^{S}_{y'y'z'},\\
\chi^{S}_{z'x'x'}=\chi^{S}_{z'y'y'}.
\end{gathered}
\tag{7}
$$

To determine the independent components of the tensors $\chi^{S}_{ijk}, \chi^{S}_{i'j'k'}, \chi^{Q}_{ijkl}$, we have taken into account their symmetry in the indices of the pump field; in this way we include the possibility that the frequency of pump radiation ω may lie in the semiconductor absorption band.

Knowing the form of the tensors (5)–(7), by making use of expressions (2)–(4) we can determine the angular dependences of the p- and s-polarized components of the vector $\mathbf{P}(2\omega)$ for the volume and surface layers of the (111) and (001) planes for arbitrary polarization of the pump radiation. The corresponding isotropic (i.e., φ-independent) and isotropic components of $\mathbf{P}(2\omega)$ are presented in Tables I–IV. In these tables we make use of the following notation: χ^{Q}_{ijkl} are the components of the volume quadrupole susceptibility tensor in the crystallographic coordinate system; χ^{S}_{ijk} are the components of the surface susceptibility tensor in the (001) plane relative to the crystallographic coordinate system; $\chi^{S}_{i'j'k'}$ are the components of (111) plane surface susceptibility tensor in the $x'y'z'$ coordinate system; l is the polarization index of the SH radiation; E is the amplitude of the pump field in the nonlinear medium; φ_2, ϑ_2 are the angles between the surface normal and the wave vectors of this SH and pump respectively; ψ is the polarization angle for the pump radiation in the nonlinear medium; k is the modulus of the wave vector of the pump radiation in the nonlinear medium; φ is the angle of rotation of the crystal in the laboratory system of coordinates. The nonlinear polarization at a frequency of 2ω has an analogous form for similar crystallographic planes in centrosymmetric crystals of the class 432.

ISOLATING THE SURFACE CONTRIBUTION

As is clear from Table II, there is no anisotropy in the second harmonic generation for the (001)-plane layer near the surface, since for any angle ψ determining the polarization of the pump within the nonlinear medium, the anisotropic component of $P^{S}(2\omega) = 0$. For $\psi = 0$, i.e., for a p-polarized pump, the isotropic component of the s-polarized component $P^{S}(2\omega)$ also reduces to zero; consequently, there is no surface contribution to $I^{2\omega}_{p,s}(\varphi)$ for the plane (001). This circumstance is a consequence of the presence of a fourfold axis of symmetry in the point group $4m$. In its turn, the presence of an odd-order axis of axis of symmetry in the point group $3m$ for the plane (111) for $\psi = 0$ causes the anisotropic component to appear in the near-surface layer when inversion symmetry is destroyed (Table I):

$$P^{S}_{p,s}(2\omega) = -\chi^{S}_{x'x'x'} E^2 \cos^2 \vartheta_2 \sin 3\varphi,$$

where ϑ_2 is the angle between the normal and the wave vector $\mathbf{k}$ of the transmitted pump wave and E is the field intensity of the pump within the nonlinear medium. The isotropic component $P^{S}_{p,s}(2\omega) = 0$.

The volume quadratic contribution to the anisotropic s-polarized SH is present for p-polarized reflection of the pump by both planes. For $\psi = 0$, from Tables III and IV it follows that the volume polarization on the (001) face equals

$$P^{Q}_{p,s}(2\omega) = -{}^{1}/_{4}[\chi^{Q}_{xxxx} - 2\chi^{Q}_{xxyy} - \chi^{Q}_{xyxy}] kE^2 \cos^2 \vartheta_2 \sin \vartheta_2 \sin 4\varphi$$

and on the (111) face

$$P^{Q}_{p,s}(2\omega) = -\sqrt{2}/6 [\chi^{Q}_{xxxx} - 2\chi^{Q}_{xxyy} - \chi^{Q}_{xyxy}] \times kE^2 (1 - 3\sin^2 \vartheta_2) \cos \vartheta_2 \sin 3\varphi,$$

TABLE I. Components of the surface nonlinear polarization for centrosymmetric crystals of classes $m3m$ and 432

l	$P^{s}_{l}(2\omega)$ (111)	
	Isotropic	Anisotropic
p	$E^2[-\chi^{S}_{x'x'z'} \sin 2\vartheta_2 \cos^2\psi \cos\varphi_2 + \{\cos^2\psi$ $(\chi^{S}_{z'z'z'} \sin^2\vartheta_2 + \chi^{S}_{z'x'x'} \cos^2\vartheta_2$ $+ \chi^{S}_{z'x'x'} \sin^2\psi\} \sin\varphi_2]$	$E^2 \chi^{S}_{x'x'x'} \{\cos^2\vartheta_2 \cos^2\psi \cos 3\varphi$ $- \sin^2\psi \cos 3\varphi - 2\cos\vartheta_2 \cos\psi \sin\psi$ $\times \sin 3\varphi\} \cos\varphi_2$
s	$E^2(-2\chi^{S}_{x'x'z'} \sin\vartheta_2 \sin\psi \cos\psi)$	$E^2(-\chi^{S}_{x'x'x'}) \{\cos^2\vartheta_2 \cos^2\psi \sin 3\varphi$ $- \sin^2\psi \sin 3\varphi + 2\cos\vartheta_2 \cos\psi \sin\psi$ $\times \cos 3\varphi\}$

TABLE II. Components of the surface nonlinear polarization for centrosymmetric crystals of classes $m3m$ and 432

l	$P_l^s(2\omega)$ (001)	
	Isotropic	Anisotropic
p	$E^2[-\chi^S_{xzx}\sin 2\vartheta_2\cos^2\psi\cos\varphi_2 + \{(\chi^S_{zzz}\sin^2\vartheta_2 + \chi^S_{zxx}\cos^2\vartheta_2)\cos^2\psi + \chi^S_{zxx}\sin^2\psi\}\sin\varphi_2]$	0
s	$E^2(-2\chi^S_{xzx}\sin\vartheta_2\sin\psi\cos\psi)$	0

TABLE III. Components of the volume polarization of centrosymmetric crystals of classes $m3m$ and 432

l	$P_l^Q(2\omega)$ (111)	
	Isotropic	Anisotropic
p	$E^2k[\{\cos^2\psi\,[{}^1/_6\sin\vartheta_2\cos^2\vartheta_2(-\chi^Q_{xxxx} + 2\chi^Q_{xxyy} + 7\chi^Q_{xyxy}) + {}^1/_3\sin^3\vartheta_2(\chi^Q_{xxxx} - 2\chi^Q_{xxyy} + 2\chi^Q_{xyxy})]] + {}^1/_6\sin^2\psi\sin\vartheta_2 \times (\chi^Q_{xxxx} - 2\chi^Q_{xxyy} + 5\chi^Q_{xyxy})\}\cos\varphi_2 + \{\cos^2\psi\,[{}^1/_3(\chi^Q_{xxxx} - 2\chi^Q_{xxyy} + 2\chi^Q_{xyxy}) \times \cos^3\vartheta_2 - {}^1/_3(-\chi^Q_{xxxx} + 2\chi^Q_{xxyy} + 4\chi^Q_{xyxy})\sin^2\vartheta_2\cos\vartheta_2] + \sin^2\psi\cdot{}^1/_3 \times (\chi^Q_{xxxx} - 2\chi^Q_{xxyy} + 2\chi^Q_{xyxy})\cos\vartheta_2\}\sin\varphi_2]$	$E^2k\cdot\frac{\sqrt{2}}{6}(\chi^Q_{xxxx} - 2\chi^Q_{xxyy} - \chi^Q_{xyxy}) \times \{[\cos^2\psi(\cos^3\vartheta_2 - 2\sin^2\vartheta_2\cos\vartheta_2) \times \cos 3\varphi - \sin^2\psi\cos\vartheta_2\cos 3\varphi - 2\cos\psi \times \sin\psi\cos 2\vartheta_2\sin 3\varphi]\cos\varphi_2 + {} + [\cos^2\psi\cos^2\vartheta_2\sin\vartheta_2\cos 3\varphi - \sin^2\psi \times \sin\vartheta_2\cos 3\varphi - \sin\psi\cos\psi\sin 2\vartheta_2 \times \sin 3\varphi]\sin\varphi_2\}$
s	$E^2k\sin\vartheta_2\cos^2\vartheta_2\sin 2\psi\cdot{}^1/_6(-\chi^Q_{xxxx} + 2\chi^Q_{xxyy} + \chi^Q_{xyxy})$	$E^2k\cdot\frac{\sqrt{2}}{6}(\chi^Q_{xxxx} - 2\chi^Q_{xxyy} - \chi^Q_{xyxy}) \times [\cos^2\psi(2\sin^2\vartheta_2\cos\vartheta_2 - \cos^2\vartheta_2) \times \sin 3\varphi + \sin^2\psi\cos\vartheta_2\sin 3\varphi - 2\cos\psi\sin\psi\cos 2\vartheta_2\cos 3\varphi]$

TABLE IV. Components of the surface nonlinear polarization for centrosymmetric crystals of classes $m3m$ and 432

l	$P_l^Q(2\omega)$ (001)	
	Isotropic	Anisotropic
p	$E^2k\,[\{\cos^2\psi\,[{}^1/_4\sin\vartheta_2\cos^2\vartheta_2(3\chi^Q_{xxxx} - 6\chi^Q_{xxyy} + \chi^Q_{xyxy}) + \sin^3\vartheta_2\chi^Q_{xyxy}] + \sin^2\psi\sin\vartheta_2\cdot{}^1/_4(\chi^Q_{xxxx} - 2\chi^Q_{xxyy} + 3\chi^Q_{xyxy})]\}\cos\varphi_2 + \{\cos^2\psi\,[\chi^Q_{xyxy} \times \cos^3\vartheta_2 - \sin^2\vartheta_2\cos\vartheta_2(\chi^Q_{xxxx} - 2\chi^Q_{xxyy})] + \chi^Q_{xyxy}\cos\vartheta_2\sin^2\psi\}\sin\varphi_2]$	$E^2k\,[{}^1/_4(\chi^Q_{xxxx} - 2\chi^Q_{xxyy} - \chi^Q_{xyxy}) \times (\cos^2\psi\cos^2\vartheta_2\sin\vartheta_2\cos 4\varphi - \sin^2\psi \times \sin\vartheta_2\cos 4\varphi + 2\sin 2\vartheta_2\cos\psi\sin\psi \times \sin 4\varphi)]\cos\varphi_2$
s	$E^2k\cos\vartheta_2\sin\vartheta_2\cos\psi\sin\psi\cdot{}^1/_2(\chi^Q_{xxxx} - 2\chi^Q_{xxyy} - \chi^Q_{xyxy})$	$E^2k{}^1/_4(\chi^Q_{xxxx} - 2\chi^Q_{xxyy} - \chi^Q_{xyxy}) \times \{\cos^2\psi\sin\vartheta_2\cos^2\vartheta_2\sin 4\varphi - \sin^2\psi \times \sin\vartheta_2\sin 4\varphi - 2\sin 2\vartheta_2\cos\psi\sin\psi \times \cos 4\varphi\}$

where k is the wave vector of the transmitted pump wave. The isotropic volume component for both planes equals zero. We note that the volume component for both planes, (111) and (001), can be expressed by using the same combination of components of the tensor χ^Q. This implies that the amplitude values of the anisotropic volume components or both faces with the assumed geometry coincide up to a numerical factor; at the same time, the contribution from the layer near the surface for the (001) plane is absent. These symmetry properties of the nonlinear polarization also allow us to separate out the surface contribution for the (111) plane by comparing the amplitude values of the anisotropic s-polarized SH for the two faces in the presence of a p-polarized pump.

For experimental estimates of the magnitude of the surface contribution we must pass from the nonlinear polarization $P(2\omega)$ to the SH field $E(2\omega)$. This can be done by taking advantage of the results of Ref. 12, in which the value of $E(2\omega)$ was obtained for radiation reflected from a semiinfinite nonlinear medium:

$$E_{p,s}^{V}(2\omega) = -\frac{4\pi}{\varepsilon(2\omega)-\varepsilon(\omega)}\,\frac{\varepsilon^{1/2}(2\omega)\cos\varphi_2-\varepsilon^{1/2}(\omega)\cos\vartheta_2}{\varepsilon^{1/2}(2\omega)\cos\varphi_2+\cos\vartheta_0}P_s^{Q}(2\omega) \qquad (8)$$

at whose surface is an infinitely thin nonlinear film; this calculation takes into account the limiting condition (4) by using a model layer with broken inversion symmetry:

$$E_{p,s}^{S}(2\omega)=\frac{i8\pi\omega/c}{\varepsilon^{1/2}(2\omega)\cos\varphi_2+\cos\vartheta_0}P_s^{S}(2\omega), \qquad (9)$$

where φ_2 is the angle between the normal to the boundary surface and the wave vector $\mathbf{k}_2$ of the transmitted second harmonic wave. It is obvious that experimental estimates based on such a crude model of the transition layer can have only a semiquantitative character.

The intensity of the anisotropic SH for the (111) plane is determined by the expression

$$I_{p,s}^{2\omega}=\frac{c}{8\pi}\Bigg|\frac{4\pi\omega c^{-1}E^2}{\varepsilon^{1/2}(2\omega)\cos\varphi_2+\cos\vartheta_0}\Big[-2\chi_{x'x'x'}\cos^2\vartheta_2 + \sqrt{2}/6\,(\chi_{xxxx}-2\chi_{xxyy}-\chi_{xyxy}) \times(1-3\sin^2\vartheta_2)\cos\vartheta_2\varepsilon^{1/2}(\omega) \times\frac{\varepsilon^{1/2}(2\omega)\cos\varphi_2-\varepsilon^{1/2}(\omega)\cos\vartheta_2}{\varepsilon(2\omega)-\varepsilon(\omega)}\Big]\sin 3\varphi\Bigg|^2 = I_{p,s}^{2\omega}(111)\sin^2 3\varphi. \qquad (10)$$

For reflection of radiation from the (001) plane, the intensity of the anisotropy SH has the form

$$I_{p,s}^{2\omega}=\frac{c}{8\pi}\Bigg|\frac{4\pi\omega c^{-1}E^2}{\varepsilon^{1/2}(2\omega)\cos\varphi_2+\cos\vartheta_0}\Big[\frac{\varepsilon^{1/2}(\omega)}{4}(\chi_{xxxx}-2\chi_{xxyy}-\chi_{xyxy}) \times\sin\vartheta_2\cos^2\vartheta_2 \times\frac{\varepsilon^{1/2}(2\omega)\cos\varphi_2-\varepsilon^{1/2}(\omega)\cos\vartheta_2}{\varepsilon(2\omega)-\varepsilon(\omega)}\Big]\sin 4\varphi\Bigg|^2 = I_{p,s}^{2\omega}(001)\sin^2 4\varphi. \qquad (11)$$

In expressions (10), (11), we denote by $I_{p,s}^{2\omega}(111)$ and $I_{p,s}^{2\omega}(001)$ the amplitude values of the angular dependence of $I^{2\omega}(\varphi)$ for the respective planes. Then for the ratio of the surface contribution $I^S(111)$ to the volume contribution $I^V(111)$ for the plane (111) we have

$$\sigma_{p,s}^{\pm}=\frac{I^S(111)}{I^V(111)}=\left|\pm\frac{3\sin\vartheta_2\cos\vartheta_2}{2\sqrt{2}(1-3\sin^2\vartheta_2)}\left(\frac{I_{p,s}^{2\omega}(111)}{I_{p,s}^{2\omega}(001)}\right)^{1/2}-1\right|^2. \qquad (12)$$

Since the volume contribution to the nonlinear polarization for the (111) plane differs from the analogous contribution for the (001) plane only by a numerical factor, we can also obtain $I^S(111)$ from expression (12). We emphasize, however, that we have not achieved a unique separation of the surface and volume contributions. This lack of uniqueness, which arises in (12) from the plus or minus sign before the first term, is related to the fact that, corresponding to expression (11), we determine experimentally only the absolute magnitude of the Raman component of the volume tensor $|\chi_{xxxx}^Q-2\chi_{xxyy}^Q-\chi_{xyxy}^Q|$, when we measure the SH intensity from the (001) plane, and not is sign. However, in expression (10) the terms inside the modulus sign can interfere, by virtue of which the resulting SH intensity for the (111) component will be determined by the signs of these terms. In the general case, for complex values of the nonlinear susceptibility we must take into account still more carefully the mutual phase shift between the individual terms of the nonlinear polarization in expression (10).

POLARIZATION SELECTION RULES FOR GENERATING A REFLECTED SH; *s-s* FORBIDDENNESS

It is clear from Tables I–IV that for s-polarized pump radiation (the angle $\psi=\pi/2$) the isotropic s-component of the nonlinear polarization vector equals zero. This implies that when the nonlinear interaction takes place in the s-s geometry, there is no isotropic SH for the crystals we are studying, i.e., the classes $m3m$ and 432; this applies to the surface dipole and volume quadrupole SH to the same degree. Furthermore, in Ref. 13 we showed the correctness of this selection rule for a nonlinear, noncentrosymmetric layer of arbitrary symmetry. Thus, s-s forbiddenness is a very strong selection rule, related in essence to the assumption of a smooth and optically homogeneous boundary between two media. However, in experiments on generation of reflected SH the isotropic component $I_{s,s}^{2\omega}$ is often detected. The reason for allowing s-s radiation, connected with roughness and surface inhomogeneity, will be discussed below.

EXPERIMENTAL RESULTS

To determine the surface contributions, we investigated the angular dependence of the reflected intensity of the s-polarized SH for a p-polarized pump, i.e., $I_{p,s}^{2\omega}(\varphi)$, the (111) and (100) planes of germanium. The surface of the (111) face was obtained by cleaving along a crystal plane, in order to exclude the creation of a damaged layer near the surface which could arise from chemical or abrasive polishing of the samples. As for the samples with (100) reflection planes, we

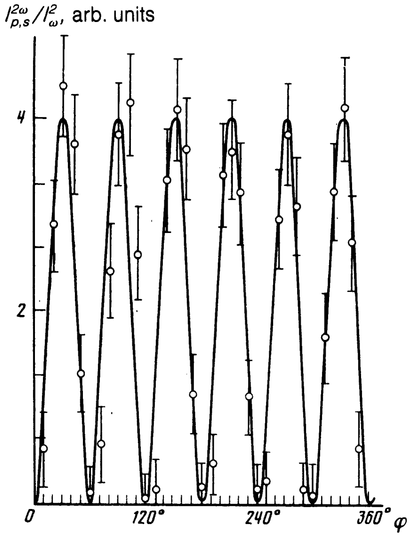

FIG. 3. Angular dependence of $I^{2\omega}_{p,s}(\varphi)/I^2_\omega$, the normalized intensity of s-polarized SH light from a cleaved (111) surface of germanium, for reflected p-polarized pump radiation (I_ω is the pump radiation intensity); O—experimental values; continuous curve—the function $(a \sin 3\varphi)^2$.

used germanium films whose surfaces were prepared by the dynamic polishing method.

Generation of anisotropic reflected SH was observed when radiation from a pulsed single-mode Nd^{3+}-YAG laser was incident on the surface of single crystal n-Ge, whose resistivity was $\rho = 3\Omega$-cm. The radiation parameters of the pump were as follows: wavelength $\lambda = 1064$ nm, pulse length $\tau \sim 20$ nsec, pulse repetition rate $\nu = 12.5$ Hz, energy density per pulse $W \sim 30$ mJ/cm^2, which is several times lower than the threshold energy density for laser annealing or generation of periodic surface structures. The angle of incidence ϑ_0 was $\sim 60°$, which is optimal for observation of reflected SH.[15] The sample could be rotated on an axis perpendicular to the reflection plane, which to a high degree of accuracy passed through the center of the spot of pump radiation. SH radiation with $\lambda = 532$ nm was collected with a condensor system at the entrance slit of a double monochromator, at whose exit it was recorded by a system consisting of a photomultiplier and velocity-gated analog-digital converter.

In Fig. 3, the dependence $I^{2\omega}_{p,s}(\varphi)$ is displayed for the (111) plane, normalized to the square of the pump power I^2_ω. The angular dependence is well approximated by the harmonic function $(a \sin 3\varphi)^2$ and has seven maxima as we rotate the sample through an angle $\varphi = 2\pi$.

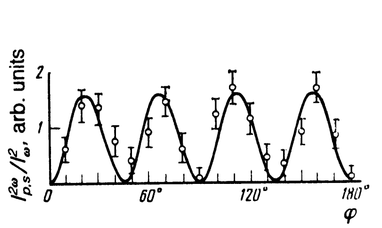

FIG. 4. Angular dependence of $I^{2\omega}_{p,s}(\varphi)/I^2_\omega$ for the (100) surface of germanium; O—experimental values; continuous curve—the function $(b \sin 4\varphi)^2$.

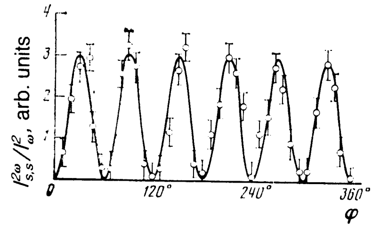

FIG. 5. Angular dependence of $I^{2\omega}_{p,s}(\varphi)/I^2_\omega$ for the (111) plane of an epitaxial film of silicon; O—experimental values; continuous curve—the function $(c \sin 3\varphi)^2$.

Analogous dependence for the (100) plane using the same vertical scale is displayed in Fig. 4. This dependence also contains no isotropic component, in correspondence with Table IV and is approximated by the function $(b \sin 4\varphi)^2$. By measuring these angular dependences, the average amplitude values $I^{(2\omega)}_{p,s}(111)$ and $I^{2\omega}_{p,s}(100)$ can be determined. Substituting the amplitudes obtained in (12) and taking into account that for germanium $\varepsilon(\omega) = 18.9 + 1.02i$ and $\varepsilon(2\omega) = 19.3 + 21.1i$,[16] we can estimate the minimum surface contribution to the generation of reflected SH for a cleaved surface. The corresponding calculations yield a value $\sigma^+_{p,s} \approx 0.29$. The magnitude of the tensor components corresponding to SH generation by the surface and volume, also can be estimated: $\chi_{x'x'x'} \sim 4.5 \times 10^{-15}$ esu, $|\chi_{xxxx} - 2\chi_{xxyy} - \chi_{xyxy}| \sim 5 \times 10^{-13}$ esu.

To verify that the s-s forbiddenness condition is fulfilled and explain the lifting of this condition, we used an s-polarized pump and investigated the angular dependence of the intensity of reflected s-polarized SH for the (111) surface of an epitaxial silicon film. The surface of the epitaxial film of silicon grown on a silicon substrate was an extremely high-quality homogeneous plane. The dependence of $I^{2\omega}_{s,s}(\varphi)$ for such a film is shown in Fig. 5. In agreement with s-s forbiddenness, this dependence does not contain an isotropic component, and is approximated by a curve of the form $(c \sin 3\varphi)^2$. In order to change the surface topography, the epitaxial films were etched for several seconds in an SR-4 solution, which led to the appearance of roughness on a submicron scale. The dependence of $I^{2\omega}_{s,s}(\varphi)$ for such a inhomogeneous silicon surface is shown in Fig. 6, from which it is clear that a significant isotropic component has appeared in the SH angular intensity, while the anisotropic contribution

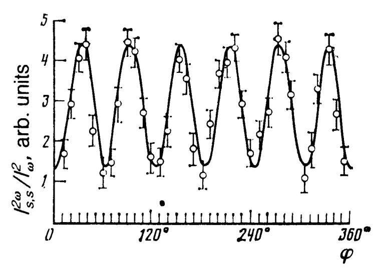

FIG. 6. Angular dependence $I^{2\omega}_{p,s}(\varphi)/I^2_\omega$ for the (111) surface of an epitaxial film of silicon exposed to a chemical etch in CR-4 solution; O—experimental values. The appearance of the forbidden isotropic component is visible. The continuous curve is the function $[h + (c \sin 3\varphi)^2]$.

remains practically unchanged. This angular dependence can be approximated by a function of the form $[h + (c \sin 3\varphi)^2]$. Thus, the generation of roughness of the surface by etching and the corresponding optical inhomogeneity of the boundary surface can result in breaking of the *s-s* forbiddenness and the appearance of an isotropic SH in the nonlinear interaction geometry under study here.

CONCLUSIONS

The analysis we have carried out of the anisotropy in the intensity of reflection SH in crystals of class $m3m$ and 432 shows the possibility in principle of separating out the nonlinear-optical contribution from the layer near the surface.

Experimental investigation of a cleaved surface layer in germanium allows us to estimate the minimum value of the surface contribution with respect to the volume as several tens of percent. The question of lack of uniqueness in determining the contribution from the surface requires further study.

Investigation of the polarization selection rules for the process of reflection SH generation allowed us to establish some reasons for the lifting of the *s-s* forbiddenness, connected with the surface topography. Based on the measurement of the magnitude of the isotropic SH, a nonlinear-optical method can be developed for remote operational control of the micro-roughness of the surfaces of metals and semiconductors.

In conclusion, the authors are grateful to L. V. Keldysh for organizing the work and for valuable comments in the course of its execution. Very useful to us were discussions of the results and talks with P. V. Elyutin and N. I. Koroteev.

[1]Gigantskoye Kombinatsionnoe Rasseyanie (Giant Raman Scattering), translated from English; edited by V. M. Agranovich. M.: Mir, 1984.
[2]O. A. Aktsipetrov, N. N. Akhmedeev, E. D. Mishina and V. R. Novak, Pis'ma Zh. Eksp. Teor. **37**, 175 (1983) [JETP Lett. **37**, 207 (1983)].
[3]O. A. Aktsipetrov, E. D. Mishina and A. V. Petukhov, Pis'ma Zh. Eksp. Teor. Fiz. **37**, 592 (1983) [JETP Lett. **37**, 707 (1983)].
[4]O. A. Aktsipetrov and E. D. Mishina, Dok. Akad. Nauk **274**, 62 (1984) [Sov. Phys. Dokl. **29**, 37 (1984)].
[5]H. W. Tom, T. F. Heinz and Y. R. Shen. Phys. Rev. Lett. **51**, 1983 (1983).
[6]T. F. Heinz, M. M. Loy and W. A. Thompson, Phys. Rev. Lett. **54**, 63 (1985).
[7]O. A. Aktsipetrov, I. M. Baranova and D. A. Esikov,Tezisy Dokladov XII Vsesoyuznoi Konferentstii po Kogerentnoi i Nelineinoi Optiki (Abstracts from the XII All-Soviet Conference on Coherent and Nonlinear Optics), Moscow 1985, part 1, p. 374.
[8]S. Kelykh, Nelineinaya Molekulyarnaya Optika (Nonlinear Molecular Optics), Nauka, Moscow (1981).
[9]L. D. Landau and E. M. Lifshitz, Elektrodinamika Sploshnykh Sred (Electrodynamics of Continuous Media, Pergamon, Oxford, 1960), Nauka, Moscow, 1982.
[10]B. K. Vainshtein, V. M. Fridkin and V. L. Indenbom, Sovremennaya Kristallografiya (Modern Crystallography), V. 2: Struktura Kristallov (Crystal Structure), Nauka, Moscow (1979).
[11]S. A. Akhmanov, V. I. Emel'yanov, N. I. Koroteev and V. N. Seminogov, Usp. Fiz. Nauk **147**, 675 (1985) [Sov. Phys. Usp. **28**, 1084 (1985)].
[12]N. Bloembergen and P. S. Pershan, Phys. Rev. **128**, 606 (1962).
[13]O. A. Aktsipetrov, N. N. Akhmedeev, N. N. Baranova, E. D. Mishina and V. R. Novak, Zh. Eksp. Teor. Fiz. **89**, 911 (1986) [Sov. Phys. JETP **62**, 524 (1986)].
[14]J. F. Young, J. S. Preston, H. M. Van Driel and J. E. Sipe, Phys. Rev. B **27**, 1155 (1983).
[15]N. Bloembergen, R. K. Change and S. S. Jha, Phys. Rev. **127**, 813 (1968).
[16]G. T. Boyd, T. Russing, I. R. R. Leite and Y. R. Shen, Phys. Rev. B **30**, 519 (1984).

Translated by Frank J. Crowne