Electronic structure, transport, and phase change in Cu$_2$GeTe$_3$

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Cu$_2$GeTe$_3$, (CGT) is expected as a promising candidate for advanced fast nonvolatile random-access-memory devices due to several preferable characteristics such as short crystallization time, long-term data-retention properties, and reduced amorphization power requirements over standard PCMs fabricated from GeTe-Sb$_2$Te$_3$ (GST) pseudo-binary alloys. The most interesting feature of CGT is that it has 4 $s$-$p$ electrons per atom and thus undergoes tetrahedral bonding, exhibiting a chalcopyrite like structure with $sp^3$ bonding in the crystalline phase. As $sp^3$ tetrahedral bonding is known generally to be very rigid, the mechanism of the reversible PC in CGT is of fundamental interest. Another outstanding question is the origin of the orders-of-magnitude higher resistivity of the amorphous phase. To provide insight into these important questions, we have investigated the electronic structure and chemical bonding in CGT by means of bulk-sensitive hard X-ray photoelectron spectroscopy, and DFT calculations to clarify the problem. We have also investigated the electric conduction properties and their changes in correlation with electronic structure changes during the annealing process.

The combination of theory and experiment has yielded a consistent model for the PC mechanism in which Te 5$s$ lone pair formation in the amorphous phase induces the enhanced participation of Cu 3$d$ states in the bonding in an interaction with the empty Te 4$d$ orbitals. In addition to this, anomalously fast diffusion of Cu atoms in the amorphous matrix is likely to be another key to the fast PC switching. The temperature dependence of the conductivity in as-deposited films is well reproduced by adopting Davis-Mott model proposed for disordered semiconductors. [1] Annealing behavior of the transport and spectroscopic data are consistently analyzed on the basis of the same D-M model. The transport is changed from conduction in the extended states in the amorphous to metallic conduction in a crystalline degenerate semiconductor via hopping conduction in disorder-induced tail state in the defective crystalline semiconductor. The high resistance in the $a$-phase which certifies a clear contrast with low resistance in the $c$-phase is due to the Fermi level pinning in the amorphous-phase at the mid-gap defect band.

The present work is a result of collaborations involving groups of JAEA, Tohoku University, AIST, and Cambridge University.

A combined x-ray absorption and ab-initio study of the local structure of Ga$_2$Te$_3$, a phase-change alloy without resonant bonding

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The large optical contrast in conventional phase-change alloys typified by the GeTe-Sb$_2$Te$_3$ (GST) alloys is thought to arise from the formation of resonant bonds in the octahedrally-coordinated crystalline phase and the concomitant rise in polarizability. Recently it was found that the tetrahedrally bonded material Ga$_2$Te$_3$ displays a similarly large property contrast, undergoes low-energy switching, and has a very low thermal conductivity in the crystalline phase, an attribute also shared by crystalline GST. As resonant bonding has been held to be behind these properties in the GST phase-change alloys, the switching mechanism in Ga$_2$Te$_3$ has remained an open question. Here we present a combined density-functional theory and x-ray absorption study of the local structure of Ga$_2$Te$_3$ that explores the bonding mechanisms in the crystalline and amorphous phases and proposes a novel model for the switching process. The results demonstrate that the efficient switching seen in Ga$_2$Te$_3$ can be ascribed to the presence of primary and secondary bonding in the crystalline phase originating from a high concentration of Ga vacancies while in turn the structural stability of both the crystalline and amorphous phases stems from the polyvalency of Te atoms and the presence of lone-pair electrons in conjunction with the formation of like-atom bonds in the amorphous phase.

Key words: Phase Change, density-functional theory, Ga$_2$Te$_3$, vacancies, x-ray absorption

Low-power consumption optical switches using phase-change material for a large capacity photonic network system

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A small-sized, low-power consumption, high-speed optical switch is a key device for a photonic network node. A recent photonic node usually uses a liquid crystal spatial light modulator as a switching engine; however, it is bulky and has slow switching speed. The optical switch using phase-change material (PCM) is suitable for such an application because the refractive index change of PCM is very large and the transition time is less than $\mu$s. It can be very small in combination with silicon photonics. The fine processes for CMOS fabrication were used for the fabrication of the silicon base lightwave circuit on a 12-inch wafer. We have developed optically and electrically controlled optical switches, where Ge$_2$Sb$_2$Te$_5$ thin films are deposited on silicon base lightwave circuit. The switching states were successfully controlled repeatedly by light pulse illumination or current pulse injection. It should be noted that the switch has very broadband characteristics of more than 100 nm, and it can cover whole C- and L-bands which are used for optical communication systems.

Key words: Optical switch, Silicon waveguide, Phase change material, Optical communication
Deposition induced spontaneous nanostructure formation at room temperature

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Silver telluride (Ag-Te) and silver germanium telluride (Ag-GeTe) have recently attracted significant attention due to intriguing material properties such as a high thermoelectric figure of merit, phase change between amorphous and crystalline states, phase transition between crystalline phases, large magnetoresistance, and 3D topological insulating behavior. The nanostructures have been reported to be fabricated by various methods, modify the structural, electronic, thermoelectric properties, and can improve the performances of phase change, memory, and thermoelectric devices.

Electrochemical reaction is a chemical reaction that involves a redox process. The electrochemical reaction has been used to fabricate metal-semiconductor nanostructures. In contrast to the numerous reports on solution-based processes for electrochemical nanostructure fabrication, there have been only a few reports on the dry-deposition process, although the dry process serves to avoid the contamination often found in solution processes, and would provide higher quality nanostructures. In this paper, we report on a room-temperature, spontaneous growth of Ag-Te and Ag-GeTe nanostructures, via electrochemical reactions by using Ag nanoparticles as the seed; the seeds were formed by thermal annealing of a sputtered Ag film to make our method a fully dry process. We demonstrate that deposition of Te by a RF magnetron sputtering onto an Ag nanoparticle transforms it into a nanowire that mainly consists of an amorphous region with composition roughly close to Ag$_2$Te, surrounded by a Te$_x$O$_{1-x}$ shell while the deposition of GeTe transforms an Ag seed into a broccoli-like nanostructure that partly consists of polycrystalline grains of monoclinic Ag$_2$Te. We will also show dependences of the electrochemically formed nanostructures on the size of the seed Ag nanoparticles and the amount of Te or GeTe deposition.

Key words: GeTe, Te, Ag$_2$Te, nanowire, nanoparticle, electrochemical reaction, RF magnetron sputtering

Study on Structural Transformation in In$_2$O$_3$-based Oxide Thin Films

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This talk focuses on the structural transformation of amorphous In$_2$O$_3$-based thin films in the various flexible electronic devices, which is considered to induce the internal stresses or severe cracking generated between the film and flexible substrate. We discussed the structural transformation from amorphous state to polycrystalline state for In$_2$O$_3$-based thin films from two aspects: 1) crystallization during sputtering deposition; 2) crystallization during the post thermal annealing. Our results show that the typical columnar growth for sputter-deposited In$_2$O$_3$-based thin films is mainly dominated by the lateral diffusion of adatoms, and the formation of the grain boundary produces an obvious diffusion barrier, and induce a slow-down of crystallization. Whereas, the thermal-annealing induced crystallization behavior can be described by a function of annealing time and annealing temperature. Around the annealing temperatures, more nanocrystallites are observed in the inside of thin film. When the annealing temperature is obviously larger than the crystallization temperature, the growth of nuclei formed in the film surface dominates the crystallization process. The addition of the impurity elements Ga can obviously improve the crystallization temperature. These results will help to avoid the deterioration of amorphous In$_2$O$_3$-based thin films and improve the durability of the related electronic devices.

Key words: In$_2$O$_3$-based Oxides, Thermal Annealing, Crystallization, EXAFS.
Film structure evolution during metal-metal hydride phase transformation: *in-situ* diffraction study on (111) textured Pd films

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The hydrogen is known to degrade metals. In this study, however, the film structure evolution during the metal ($\alpha$) to metal hydride ($\beta$) phase transformation was observed in the (111) textured palladium (Pd) thin films. Hence, the evolution mechanism of the films was investigated using the *in-situ* X-ray diffractometry. According to the analysis results of the diffraction stress analysis, the $\beta$-phase formation during the $\alpha$-to-$\beta$ phase transformation took place at the same in-plane stress present in $\alpha$-phase, and *vice versa*. Based on this in-plane stress agreement in two phases, the mechanism of the film structure evolution was discussed. It was concluded that the cyclic $\alpha$-$\beta$ grain boundary motion during the $\alpha$-to-$\beta$ phase transformation occurred mainly along the in-plane direction and this in-plane grain boundary motion results in the film structure evolution, such as the in-plane grain growth, the lattice defect removal and the (111) texture enhancement. The conclusion also suggests that the evolution based on this mechanism takes place only on the thin film and not on the thick film or bulk case.

**Key words:** Hydrogen, Metal Hydride, Palladium, Textured Film.
Thermal conduction control in Si membrane by phonon engineering

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Thermal phonon engineering using ballisticity and wave nature of phonons brought new possibility to thermal conduction engineering. We introduce characteristic heat transfer in Si phononic nanostructures including heat focusing [1] and counter intuitive heat transfer based on wave nature of phonons [2].

We fabricated 145-nm-thick single-crystalline Si porous membranes by conventional top-down approach using electron beam lithography and measured thermal conduction in the nanostructures by a custom built micro-time-domain thermoreflectance system. We demonstrate that heat flow can be focused by using the ballisticity of thermal phonons within the mean free path: heat flux can be focused in a phononic structure with holes which aligned in a radial fashion. The fabricated structures have a slit centered at the focus or shifted. The heat dissipation times were compared among these structures and showed strong position dependence of the slit; the fastest heat dissipation was observed when the slit was located at the focus. About 7% difference can be observed even at room temperature due to long thermal phonon MFP in Si. This result is the first demonstration of heat focusing using tailored phononic structures. In the presentation, development of nanostructured Si thermoelectric material will be also presented.

Key words: phonon engineering, phononics, phonic crystal, phonon, heat transport

Recent Trends in Research on Cubic GeSbTe System as Thermoelectric Materials

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GeSbTe system is a representative phase-change material for rewritable optical data storage applications, such as CDs, DVDs, and Blu-ray discs. It possesses a unique combination of physical properties, such as a large contrast in optical reflectively and electrical conductivity between the amorphous and the cubic phases, and a rapid phase transition between both phases triggered through instantaneous heating/cooling by laser irradiation. For this reason, the relationship among structural, electronic, optical, thermal, and electrical properties of GeSbTe system has extensively been investigated either theoretically or experimentally. Such unique properties of phase-change materials could also lead to a promising candidates for thermoelectric materials, which can directly convert heat into electricity. Especially cubic GeSbTe system has been focused attention recently due to its high thermoelectric performance [1-5]. I will introduce ongoing thermoelectric research of cubic GeSbTe system in my group. Furthermore, recent trends in research on cubic GeSbTe system in the field of thermoelectric materials will be introduced in terms of relationship between the crystal structure and thermoelectric properties.

Key words: Thermoelectric, crystal structure, electrical properties, thermal conductivity, GeSbTe

Fig. 1. Crystal structure of cubic and hexagonal Ge₅Sb₂Te₅.

Ultrafast coherent phenomena in topological phase-change materials

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The interfacial phase change memory (iPCM) material, Ge-Sb-Te based superlattice structure, has shown novel (faster speed and less power-consuming) optical and electrical properties over the conventional Ge-Sb-Te alloyed structures [1]. To understand the interesting physical phenomena in iPCM material, we have investigated phonon and spin dynamics as responses to femtosecond optical pulse irradiation, which would determine the local atomic rearrangement and property of topological spin on the surface [2-11]. In this paper, we present recent updates on the ultrafast coherent phenomena in topological phase-change materials, e.g., all-optical structural analysis of iPCM using acoustic phonons and the effect of superlattice structure of iPCM on the spin dynamics using time-resolved magneto-optical Kerr-rotation (MOKE) [11]. In both experiments, near-infrared femtosecond pulses from Ti:sapphire laser (20-fs pulse duration and 830 nm wavelength) were used to conduct pump-probe ultrafast coherent spectroscopy. We demonstrate that the superlattice structure of iPCM and spin dynamics are both linked each other.

Key words: Phase-change material, Coherent phonon, Femtosecond, Spin, Topological insulator.

References
Heterogeneous Storage with Storage Class Memories and NAND Flash Memory for Big and Fast Data Processing

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Big data for prediction and fast data for real-time analysis are tightly coupled in emerging machine learning and artificial intelligence applications. Workloads diversity requires diverse storage architectures with NAND flash memory and storage class memory (SCM) such as MRAM, ReRAM and PRAM. Because SCMs are different in read/write latency, endurance, reliability and bit cost, MRAM is called memory-type SCM (M-SCM) while PRAM and ReRAM are called storage-type SCM (S-SCM). Therefore, it is necessary to properly use the appropriate SCM according to workloads’ characteristics. This paper provides performance analysis of storages with M-SCM, S-SCM and NAND flash memory. When total cost of SCM/NAND flash hybrid storage is capped by 1.5 times of NAND flash only storage, large capacity S-SCM such as PRAM shows 3 times higher performance than small capacity M-SCM for a hot workload requiring SCM. By further adding small capacity M-SCM to the S-SCM/NAND flash hybrid storage, performance of the heterogeneous storage is improved by 22%.

Key words: storage class memory, NAND flash memory, heterogeneous storage
ABSTRACT

One of the appealing possibilities of phase change random access memory (PRAM) development is the implementation of multi-level states encoding, preferably within a single cell. Such a possibility has been demonstrated recently [1,2], however, usually the required multi-level cell encoding is more complicated than the corresponding conventional two-state PRAM counterpart, and also data retention, cyclability, or energy consumption of the switching are insufficient. In this work the use of GeTe/Sb2Te3 superlattices for iPCM devices is shown to be suitable for multi-level switching. iPCM devices were fabricated with a 3 nm thick room temperature-grown Sb2Te3 seed layer and a 40 nm thick superlattice [(GeTe)2(Sb2Te3)4]8 grown at 230˚C by sputtering [3]. The contact size of the devices was varied from 50x50 to 100x100 nm. In addition to the conventional switching fabricated devices show the dependence of the appearance of additional (intermediate) levels of the device resistance on the switching pulse duration (figure 1). If the applied switching pulse is longer than ~150 ns then the switching happens in a similar manner to the conventional case, but as soon as the switching pulse becomes shorter, intermediate levels of resistance appear. Starting from the RESET state, the first intermediate resistance level can be obtained by applying 0.5–0.9 V and 20–60 ns duration pulses.

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Key words: iPCM, GeSbTe, Superlattice, phase-change switching.
Interfacial properties of Electrodes/GeCu$_2$Te$_3$ phase change material

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Recently, phase change random access memory (PCRAM) has attracted much attention as a next generation non-volatile memory since Intel and Micron start to mass production of X-point memory, which is consisted of both PCRAM and onvonic threshold switching (OTS) device. In such a memory, there are two issues because the memory cell size becomes 10-100 nm scale. One is a thermal disturbance between cells [1]. After a RESET pulse is applied to a cell, an adjacent cell unintentionally may be rewritten by Joule heat in the RESET pulse. In order to prevent the unintentional crystallization, a new phase change material with high thermal stability of amorphous state is needed. So, we have proposed GeCu$_2$Te$_3$ (GCT) phase change material for next-generation PCRAM application. GCT has higher crystallization temperature, $T_c$, (230 °C) than conventional phase change material Ge$_2$Sb$_2$Te$_5$ (GST, $T_c$ = 160 °C). Moreover, GCT has lower melting point (500 °C) than GST (630 °C) [2], a fast crystallization rate [3] and small volume change [3-4], so that GCT is expected to show excellent PCRAM memory performance. Actually, our group demonstrated that power consumption of GCT PCRAM is lower than that of GST PCRAM [5]. Second, we need to consider a contact resistance, $R_c$, between an electrode and GCT, since the total resistance, $R_T$, of GCT memory cell is dominated by the $R_c$, in range of μm-nm cell size [6]. In this study, we investigated the electrode, carrier concentration and annealing temperature dependence of $R_c$. The $R_c$ of crystalline GCT showed almost no electrode dependence, meanwhile the $R_c$ of Ni/amorphous GCT became an order of magnitude lower than W and Pt electrode. Because crystalline GCT shows metallic behavior and amorphous GCT shows semiconducting behavior. In the presentation, the electrode dependence of $R_c$ will be discussed based on hard X-ray photoemission spectroscopy (HAXPES) measurement and transmission electron microscopy (TEM) observation.

Key words: GeCu$_2$Te$_3$, contact resistivity, phase change random access memory

Phase Change Random Access Memory (PCRAM) is expected as a candidate for next generation non-volatile memory (NVM). However, the thermal stability of phase change material in amorphous phase should be improved for usage in high temperature. In our previous study, we reported that Cr-Ge-Te ternary compound, Cr$_2$Ge$_2$Te$_6$ (CGT), exhibits a high thermal stability in its amorphous phase and inverse resistance change between low resistance of amorphous and high resistance of crystalline phases, suggesting a low power consumption (low operation current) for amorphization [1]. Therefore, in this study, we fabricated memory cell device using CGT and investigated its switching properties.

CGT film was deposited on SiO$_2$ (100 nm)/Si substrate or glass substrate (Corning, Eagle-XG) by RF magnetron co-sputtering using Cr, Ge and Te pure metal targets. CGT memory cell was fabricated using FIB and lithography technique.

The temperature dependence of the resistance for CGT film was measured by two-point probe method. As-deposited and annealed CGT films were confirmed to be amorphous and crystalline phases by XRD. From these results, we confirmed inverse resistance change for CGT film between low resistance of amorphous and high resistance of crystalline phases as reported on previous study [1]. Resistive switching behavior of CGT memory cell was demonstrated by $R$-$V$ measurement. It was found that CGT memory cell can show reversible resistive switching with short pulse width of 30 ns indicating its high operation speed. In this presentation, contact resistivity change and Hall properties of CGT film will be also discussed.

**Key words**: Cr-Ge-Te, Cr$_2$Ge$_2$Te$_6$, High thermal stability.

Active-controlled plasmonic waveguides using GeSbTe superlattice.

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Developments of surface plasmon (SP) waveguides are crucial for constructing subwavelength-scale optical circuits and devices. Actively controllable plasmonic devices, which are required for optical modulations and switching and routing of information signals, are constructed by including the SP waveguides feasibilities of amplitude and/or phase modulations of electromagnetic fields in the waveguides [1-3]. In this paper, we report developments of active control SP waveguides using a phase change material, [(GeTe)2/(Sb2Te3)1]20 superlattice (GST-SL), as an active medium. GST-SL is constructed by a multiple stack of the GeTe and the Sb2Te3 layers [4]. Either a light pulse irradiation or applying an electrical pulse can induce displacements of the Ge atoms in a direction perpendicular to the adjacent Sb2Te3 layer, which cause modulations of both electrical conductivity and optical constants. Compared to the conventional Ge2Sb2Te5 (GST) alloy, the phase transition of GST-SL exhibits smaller energy consumptions, faster transition times, and larger contrasts of optical constants (i.e. refractive index and extinction coefficient) between the two phases [5]. When the GST-SL is used as a component of SP waveguide, the large change in optical constants significantly alters the propagation length and the wavelength of the SP mode, thus such waveguides function as plasmonic (optical) modulators. Two types of SP waveguides for telecom wavelength light (λ = 1.55 μm) are investigated: The first one consists of a GST-SL – Air – GST-SL structure. Computational simulations suggest that when the GST-SL is set at the RESET phase, which has lower electric conductivity and larger light attenuation, the electromagnetic field is strongly confined in the air-gap region. As the GST-SL changes to the SET phase, the confinement capability is lost and the light transmission through the waveguide is decreased. The second one consists of Metal – Insulator – GST-SL structure. In this case, phase transition of GST-SL changes the effective complex refractive index of the SP mode that is dominantly confined in the insulator layer. As the phase of GST-SL changes from the RESET to the SET, both the refractive index and the attenuation coefficient of SP decrease, therefore both the wavelength and the propagation length of SP are extended. These results suggest usability of GST-SL for constructions of active plasmonic modulators.

Key words: GeSbTe, Superlattice, Surface plasmon, Plasmonics, Waveguide

Terahertz (THz) wave is electromagnetic radiation whose photon energy is millielectron volt order. Unlike visible and infrared light, THz wave does not cause interband electronic transition yet can interact with free carrier in semiconductors. Therefore, THz spectroscopic study are powerful tool to study an insulator-to-metal phase transition in Ge-Sb-Te (GST) phase change materials as well as a surface state of topological insulators. Here we report the recent results of THz time domain spectroscopy (THz-TDS) and THz emission spectroscopy in GST alloys and \([\text{GeTe}_2/\text{Sb}_2\text{Te}_3]_n\) samples. We found that amorphous GST alloy is basically transparent for THz wave because of absence of free carrier yet crystalline GST alloys absorb THz wave due to modification of electronic structure that is caused depending on the annealing temperature. Therefore, GST alloy can be used for THz modulation application. The combination of THz-TDS and THz emission spectroscopy measurements revealed that \([\text{GeTe}_2/\text{Sb}_2\text{Te}_3]_n\) samples with the different number of multi-layer stacking possess different electronic property that might be related to topological nature and the spoiled structure due to successive stacking. In addition, we describe the surface modification in GST samples induced by intense THz pulse train derived from THz free electron laser.
Ab initio calculation of optical properties change of antimonide due to the melting

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Antimonides such as Sb$_2$Te$_3$ and InSb are used as the best candidate material for the active layer in a super-resolution optical disc. These two materials show the different types of optical properties change by the phase transition. Namely, the optical absorption of Sb$_2$Te$_3$ at a photon energy of $\epsilon_\omega=3.06$ eV decreases due to the melting, while that of InSb increases. In order to clarify the mechanism of the optical properties change and especially to understand the origin of the difference between Sb$_2$Te$_3$ and InSb, we have performed ab initio calculations about electronic and optical properties of Sb$_2$Te$_3$ and InSb for both crystalline and liquid states.

In this study, the Vienna ab initio simulation package (VASP) was used. To obtain model atomic structures for liquid state, ab initio molecular dynamics (MD) was performed. Electronic states and optical dielectric functions were calculated, considering the spin-orbit coupling effect.

The calculated results indicate that for both Sb$_2$Te$_3$ and InSb, the density of states around the Fermi level increases due to the melting, and the energy band gap opening near the Fermi level disappears. As a result, the optical properties also change drastically. The imaginary parts of dielectric functions in the crystalline state have several peaks corresponding to inter band transitions between semiconductor-like electronic states. Due to the melting, these peaks disappear, and the dielectric functions become metallic behavior to some extent. From the detailed analysis, we propose that the difference in the electronic states near the Fermi level between crystal Sb$_2$Te$_3$ and crystal InSb causes the difference in the optical absorption change due to the melting.

Key words: Ab initio calculation, optical dielectric function, density of states, phase transition, Sb$_2$Te$_3$, InSb
Fano resonance in topological insulators revealed by coherent phonon spectroscopy

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ABSTRACT

Key words: Topological insulator, Coherent phonon, Sb2Te3, Fano resonance etc.

Topological insulator (TI), a new class of quantum phase of matter, is characterized by a band gap in bulk like a normal insulator, and a metallic gapless surface states, which are protected from the backscattering [1]. TI is shown to be a promising candidate in the aspects of the application in spintronic and optoelectronic devices, since its spin is locked to their momentum orthogonally to each other. The investigation of phonon dynamics in TI is an interesting research question for understanding the fundamental electron-phonon interaction. The phonon properties in TI have been extensively studied using Raman scattering measurements [2]. Although, the electron-phonon interaction in the time domain are less understood in TI. In this work, we report on the dynamics of coherent phonon, generated by ultrashort laser pulses through the displacive excitation of coherent phonon (DECP) [3], in a prototype Sb2Te3 TI. We performed a transient reflectivity measurement on Sb2Te3 of 5 quintuple layer (QL) thick sample using a novel time-resolved pump-probe reflectivity. The transient reflectivity signal (Fig.1a) shows an oscillatory signal in combination with a non-oscillatory signal as a background. The oscillatory signal is attributed to the coherent phonon. To explore the coherent phonon dynamics in details, we have performed a discrete wavelet transform (DWT) [4] of the oscillatory signal after subtracting the non-oscillatory component. The DWT spectrum (Fig.1b) shows two strong peaks assigned to A1g1 and A1g2 phonon modes, respectively. It is interesting to note that the A1g2 phonon mode exhibits an anti-symmetric line shape in higher frequency side. Such anti-symmetric line shape is attributed to quantum interference between the discrete A1g2 phonon mode and a created Dirac Plasmon state [5], refer to as a Fano resonance [6]. We explore that the transient Fano resonance survives up to ≈1 picosecond clearly observed in DWT spectrum.

Fig.1. a, Transient pump-probe reflectivity signal. b, Time and frequency domain DWT spectrum. The A1g1 and A1g2 phonon modes are indicated, respectively.

References:
Optical modulator driven by electrical pulse-induced phase transition of [(GeTe)\(_2/(Sb_2Te_3)_1\)]\(_{20}\) superlattice

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We suggest a new design of optical modulator driven by phase transition of [(GeTe)\(_2/(Sb_2Te_3)_1\)]\(_{20}\) superlattice (GST-SL) induced by applying electrical pulses. GST-SL is a phase-change material, which has two different solid phases, namely high-resistive phase (RESET phase) and low-resistive phase (SET phase). While the structure changes from RESET to SET, refractive index and absorption coefficient change. The average chemical composition of GST-SL is same as Ge\(_2\)Sb\(_2\)Te\(_5\) alloy, however, GST-SL possesses an advantage over the GST alloy particularly in the reduction of energy consumption during phase transition and in the high-speed transition time.

We used multilayered ITO/GST-SL/ITO/Au/Cr film deposited on a Al\(_2\)O\(_3\) substrate. ITO layer have a role of the electrode as well as the optical waveguide. To induce the phase transition of GST-SL, single electrical pulses (pulse width: 500 ns) are applied to the sample between the upper ITO layer and the lower ITO layer. The voltage of the pulse was initially set as 0.2 V, and gradually increased to 4.0 V with an increment step of 0.08 V. The current value increases suddenly when the voltage reached to 3.1 V and the resistance value decreases about 200 \(\Omega\). This behavior is interpreted as the RESET to SET phase transition of the GST-SL.

To evaluate the optical modulation for the light wavelength of 1.55 \(\mu\)m, we performed a computational electromagnetic field simulation using Finite Difference Time Domain (FDTD) method. Intensity ratio of guiding mode between RESET phase and SET phase reaches to 1:13 from the FDTD calculation. Our result suggests an availability of new optical, modulating devices utilizing phase transition materials.

![Fig. 1 The schematic view of sample formation.](image)

**Key words:** Phase change, GeSbTe superlattice, Optical modulation
Current driven optical gate switch using a Ge$_2$Sb$_2$Te$_5$ thin film and an indium tin oxide heater

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We designed and fabricated compact an optical gate switch using a Ge$_2$Sb$_2$Te$_5$ (GST225) thin film and an indium tin oxide (ITO) heater. An optical switch is used for optical communication to select paths of optical signals at the network node without optical-to-electrical conversion. In recent years, optical systems in telecommunication nodes and data centers have become complicated because of increasing network traffic, where low-power consumption and small-sized optical switches are required. The optical switch using phase change material (PCM) is suitable for such an application. The refractive index change between amorphous and crystalline GST225 is very large; therefore, a compact optical switch can be realized compared to the optical switch utilizing thermo-optic effect or electro-optic effect. In addition, PCM is nonvolatile, and no power is needed for maintaining the switching state.

In this switch, a transparent ITO heater is deposited on a silicon waveguide, and GST225 thin film is formed on the heater. By injecting a short current pulse to the ITO heater, GST225 is heated and its phase is changed. When GST225 is in the amorphous state, the extinction coefficient of the refractive index is small and the light is not absorbed and propagates through a silicon waveguide. On the other hand, when it is in the crystalline state, the extinction coefficient is large, the light signal is absorbed by GST225.

The switching operation of the fabricated optical gate switch was observed. The current pulse injected into the ITO heater for amorphization was 20 mA with a pulse width of 100 ns, and that for crystallization was 12 mA with a pulse width of 100 ms. The measured average extinction ratio was 1.2 dB within the wavelength range of 1.525 to 1.625 μm.

**Key words**: Phase Change, PCM, GeSbTe, GST, Optical switch, telecommunication
Effects of Nitrogen doping on the properties of Cr-Ge-Te ternary compound film

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Phase change material (PCM), showing fast and reversible phase transition between amorphous and crystalline phase, has been extensively studied for the next generation Nonvolatile memory applications (i.e., PCRAM). Ge$_2$Sb$_2$Te$_5$ (GST) is the most mature PCM for PCRAM application, but there are still some limited properties such as thermal stability, power consumption and phase change speed problems for future PCRAM. Our group recently found an alternative PCM Cr-Ge-Te ternary compound showing unique inverse electrical behavior compared to the conventional PCMs, namely, high resistance crystalline and low resistance amorphous states. This inverse electrical property provides an extremely high resistance in crystalline state (3 order higher than crystalline GST) which can significantly reduce the amorphization energy. In this work, to further improve the thermal stability of the Cr-Ge-Te ternary compound, the effects of nitrogen doping on phase change properties of Cr-Ge-Te ternary compound have been investigated by two-point probe, X-ray diffraction (XRD), Hall measurement system and differential scanning calorimetry (DSC). We found that the crystallization temperature increased with higher N concentration, resulting a better thermal stability. It was also found that N incorporation in the Cr-Ge-Te (i.e., low resistance amorphous/high resistance crystalline) can alter it to a normal PCM. In this presentation, we will also discuss about the memory cell properties of N-doped Cr-Ge-Te PCM.

Key words: Non-volatile memory, Phase change material, Cr-Ge-Te ternary compound, N doping
GeTe nanowires are promising for enhancing the performances of the GeTe-based devices as phase change memory. GeTe nanowires have been demonstrated using Au nanoparticles as the catalyst. However, the nanowires using Ag catalyst have not been reported yet, despite the expectation for Ag-GeTe nanowire application for ECM memory and the platform of thermo-electric devices. In this paper, we demonstrate GeTe nanowire growth using Ag nanoparticles as the catalyst. We find that the nanowires consist of rhombohedral GeTe crystal phase, and are grown by a catalyst-on-bottom mode.

The GeTe nanowires were grown under Ar gas flow in a furnace with a temperature gradient; the source temperature was set to 500 or 700°C while the substrate temperature was set to 380°C. The GeTe nanowires grown at a source temperature of 700°C have relatively thick diameter ranging from 700 nm to 1500 nm, and short length ranging from 3 to 8 μm [Fig. 1(a,b)]. On the other hand, the GeTe nanowires grown at a source temperature of 500°C have relatively thin diameter ranging from 100 nm to 150 nm and long length ranging from 50 to 500 μm [Fig. 1(d,e)]. In both cases, the nanowires mainly have a rhombohedral GeTe crystalline structure [Fig. 1(c,f)] although 700°C source temperature produces an oxidized Ge region covering the rhombohedral GeTe nanowire region. No EDX signals of Ag on top of both nanowires suggest that the nanowires were grown by a catalyst-on-bottom mode.

**Key words:** GeTe, nanowire, Ag catalyst
Exploring iPCM structure by coherent folded acoustic phonons

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Interfacial phase change memory (iPCM) \cite{Simpson2011} is a potential candidate for the application for future memory technology over the conventional phase-change material of Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} alloy based PCM. Its structure and phase change mechanism have been investigated by several ways, such as, Extended X-ray Absorption Fine Structure (EXAFS) and Transmission Electron Microscopy (TEM) \cite{Momand2015}, since it was invented in 2011. However, those investigations have often been interrupted by intermixing at the interface of superlattice structures. Fortunately, the sample quality has been improved in recent several years, and it enables us to detect a new phonon mode with coherent phonon spectroscopy (CPS). In a superlattice, as shown in Fig. 1, acoustic phonon dispersion curve is folded at $\pi/D$ since the superlattice period $D$ is much larger than the lattice constant $a_0$. The dispersion curve becomes zigzag, and therefore $q=0$ folded acoustic mode can be observed in Raman and coherent phonon spectroscopy. We succeeded to observe, for the first time, its folded longitudinal acoustic (FLA) phonon in iPCM (Fig. 2), which is an evidence of superlattice structure of our sample. We conducted CPS on three samples whose GeTe thickness was varied from 0.72 to 2.15 nm to check if the frequency of FLA really depends on $D$. The FLA peak in the FT spectra showed a red shift as the GeTe thickness becomes larger. We compared peak frequency with the dispersion curve calculated by elastic continuum model, and found a good agreement between the calculation and experiment. We discuss the possible superlattice structure based on our results.

REFERENCES


Hydrodynamics of Active Colloids on GeSbTe Substrate Induced by Laser Heating

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Collective motions of colloidal particles as a nonequilibrium system have been widely studied to reproduce and model cooperative behaviors in nature, including swarm of insects, and flock of fishes and birds. Self-organizing phenomena of colloidal particles to mimic cells and microorganisms also attract much attention because elucidation and control of the mechanism will lead to nanoscale mass transport and autonomous structure formation. In this study, we propose a new experimental platform in which the driving force for particle motion is provided by its environment and memory effect in the particle-particle and particle-environment interactions is involved. Specifically, we observed the motion of polystyrene (PS) microparticles (1-2 μm in diameter) in a water layer sandwiched by two cover slips, one of which is covered with a GeSbTe thin film. By irradiation of laser pulse train, the GST film is heated and thereby a thermal convection flow, which works as the driving force for PS particles, is generated. Depending on the laser pulse fluence and the particle density, peculiar collective behaviors like “crystallization” and “flock formation” of PS particles were observed.

Key words: Colloids, collective motion, self-organization, GeSbTe.

Optical Control of Translocation Dynamics through Nanopore with Ge₂Sb₂Te₅ thin film

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The lower thermal conductivity of chalcogenide glass material Ge₂Sb₂Te₅ is potentially available for generating localized-thermal distribution in a solvent. We previously reported that the thermal property of Ge₂Sb₂Te₅ provided thermal and long-range transportation of polystyrene beads in a 2D micro-fluid channels due to heat convection induced by localized-thermal distribution. A long-range transportation technology has long been desired for biological applications, for example, cell sorting, protein detection, and DNA sensor. In this work, we demonstrate an application of Ge₂Sb₂Te₅ to a nanopore sensor device. Nanopore is a nano-scale hole on a thin solid-state membrane and used in nano-fluid devices. Translocation of proteins and DNA molecules through a nanopore and measuring ionic current blockades or fluorescence signals allows single molecule measurements due to its extremely high spatial resolution. An applied voltage is needed to translocate charged biomaterials through a nanopore and ensures its high throughput analysis, however, high electric field in a nanopore causes an extremely high speed translocation, and exceeds the limitation of time resolution for a detector. Here, we report that the combination of Ge₂Sb₂Te₅ and nanopore potentially improved the throughput by thermal transport while an optical measurement and reduced the speed with a lower applied voltage.

Key words: Ge₂Sb₂Te₅, Thermal conductivity, Nanopore, etc.
Diffusive behavior of GeSbTe coated Janus particles

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Designing the diffusive behavior and self-assembly of colloidal particles are important for fabrication of functional active materials. Janus particles (JPs) are one of the active colloidal particles which are formed with two hemispheres of different substances. Because they possess multi properties within one particle, JPs exhibit different behavior from colloidal particles that are created by uniform materials. Development of the JPs can be applicable for the variety of research fields, e.g., elucidation of dynamics of living systems, improvement of microelectromechanical systems, fabrication of photonic crystals, and enhancement of biosensing capability [1].

Many kinds of JPs coated with metal have been developed and show different movement due to the properties inherent to substances [2]. Here, we present a study of silica JPs partially coated with phase change material, GeSbTe225. In experiment, JPs were solvated in distilled water sandwiched by two indium tin oxide (ITO) coated coverslips. We report the diffusive behavior and shape of self-assembly of JPs under alternating electric field.

Key words: Janus particles, GeSbTe, Phase Change material