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Tominaga et al.(10) **Pub. No.: US 2010/0200828 A1**(43) **Pub. Date: Aug. 12, 2010**(54) **SOLID MEMORY****Publication Classification**(76) Inventors: **Junji Tominaga**, Ibaraki (JP);
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H01L 45/00 (2006.01)(52) **U.S. Cl.** **257/2; 257/E45.001**Correspondence Address:
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RESTON, VA 20195 (US)(57) **ABSTRACT**

In one embodiment of the present invention, recording and erasing of data in PRAM have hitherto been performed based on a change in physical characteristics caused by primary phase-transformation of a crystalline state and an amorphous state of a chalcogen compound including Te which serves as a recording material. Since, however, a recording thin film is formed of a polycrystal but not a single crystal, a variation in resistance values occurs and a change in volume caused upon phase-transition has placed a limit on the number of times of readout of record. In one embodiment, the above problem is solved by preparing a solid memory having a superlattice structure of thin films including Ge and thin films including Sb. The solid memory can realize the number of times of repeated recording and erasing of 10^{15} .

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(2), (4) Date: **Feb. 23, 2010**(30) **Foreign Application Priority Data**

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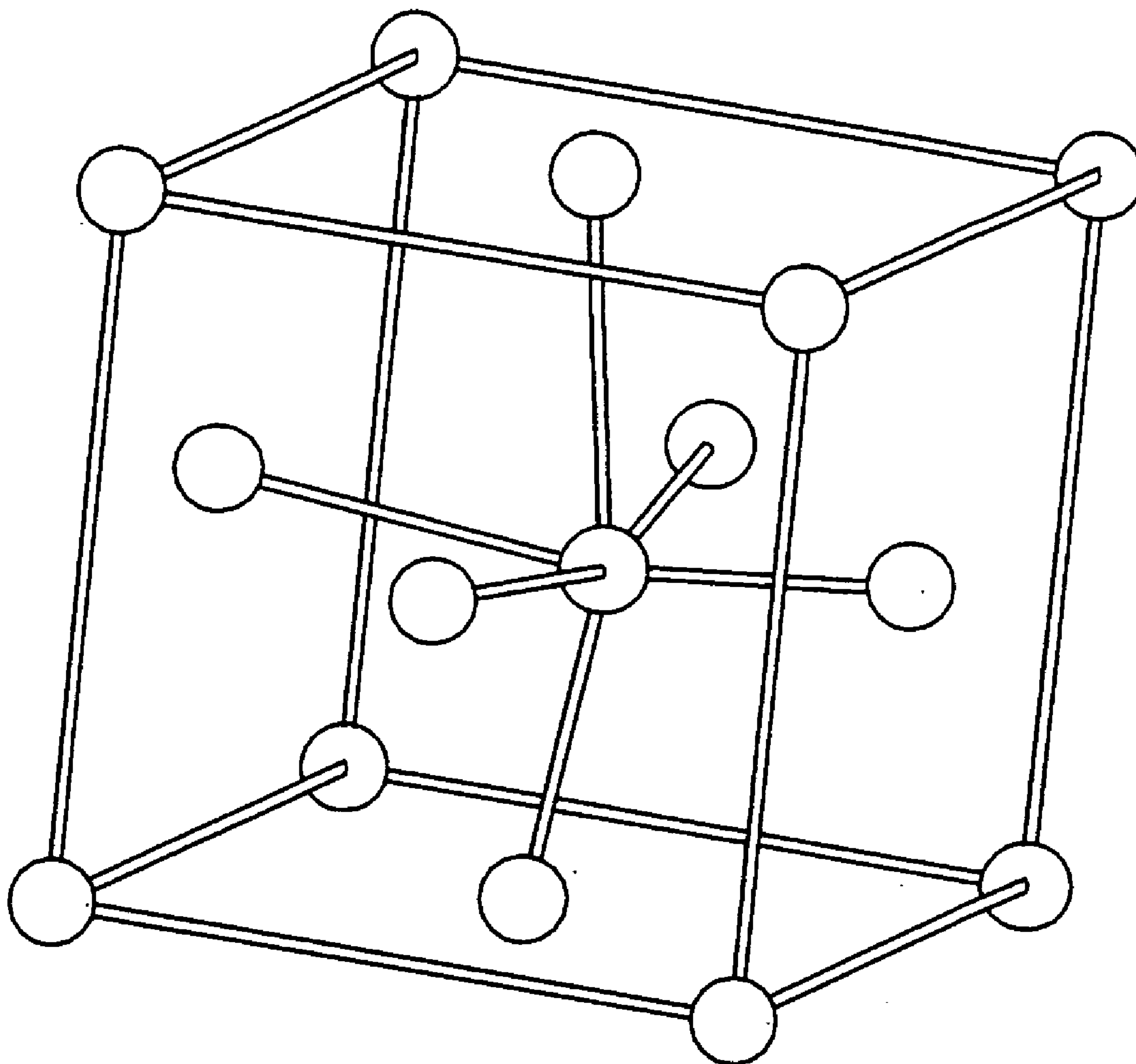
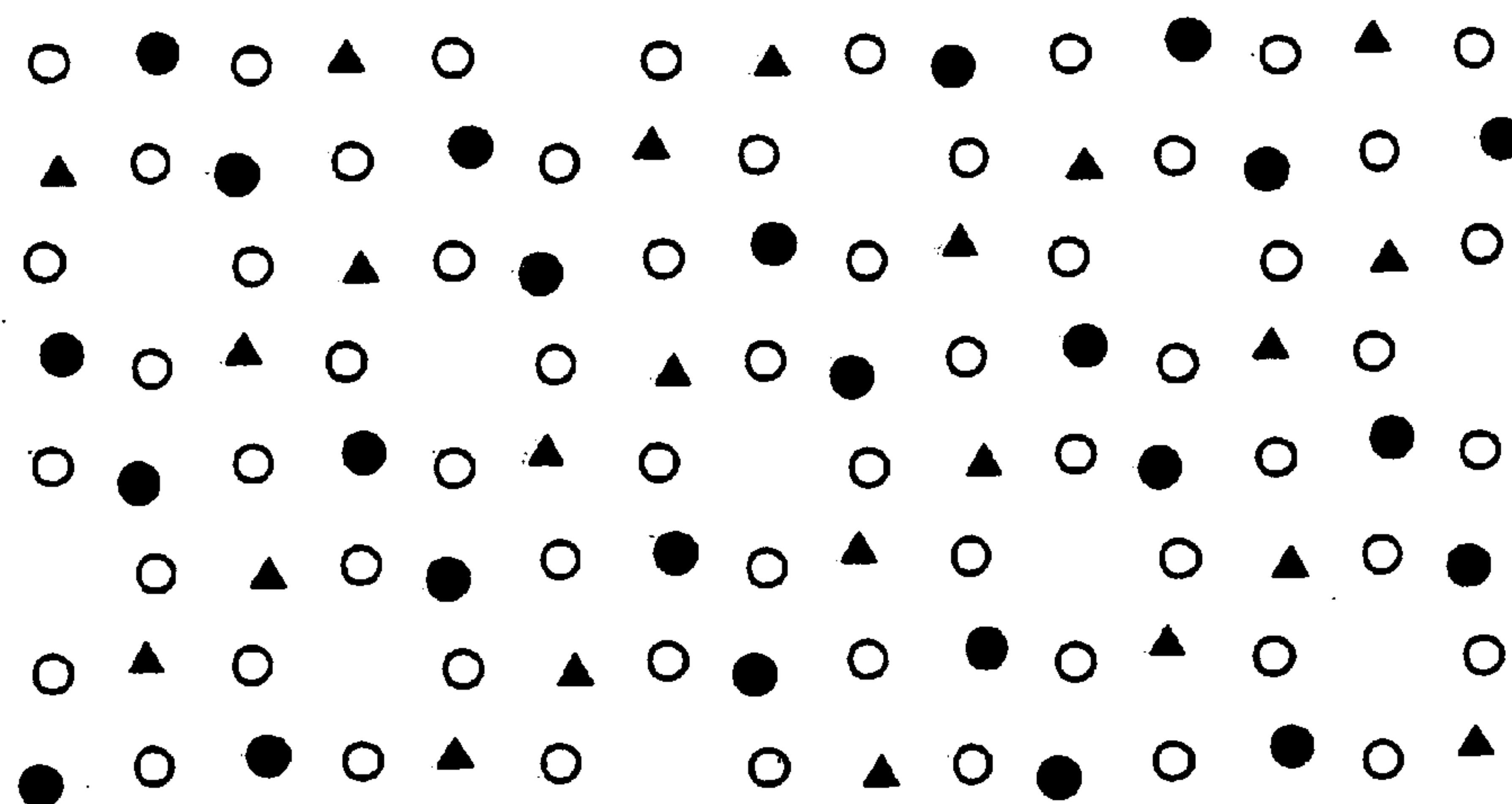
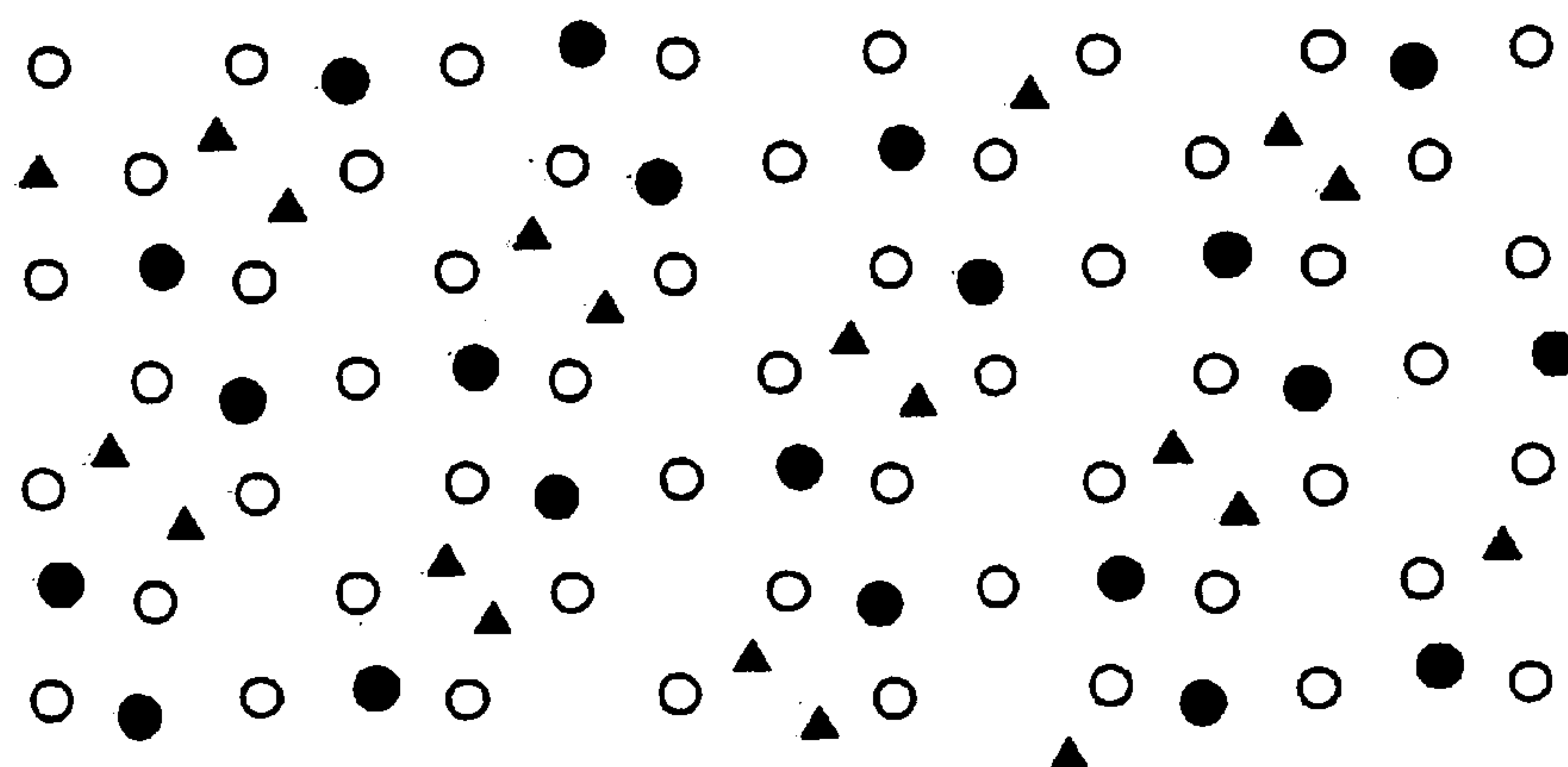


FIG. 1



White circle represents Te.
black circle represents Sb.
black triangle represents Ge.

FIG. 2



White circle represents Te.
black circle represents Sb.
black triangle represents Ge.

FIG. 3

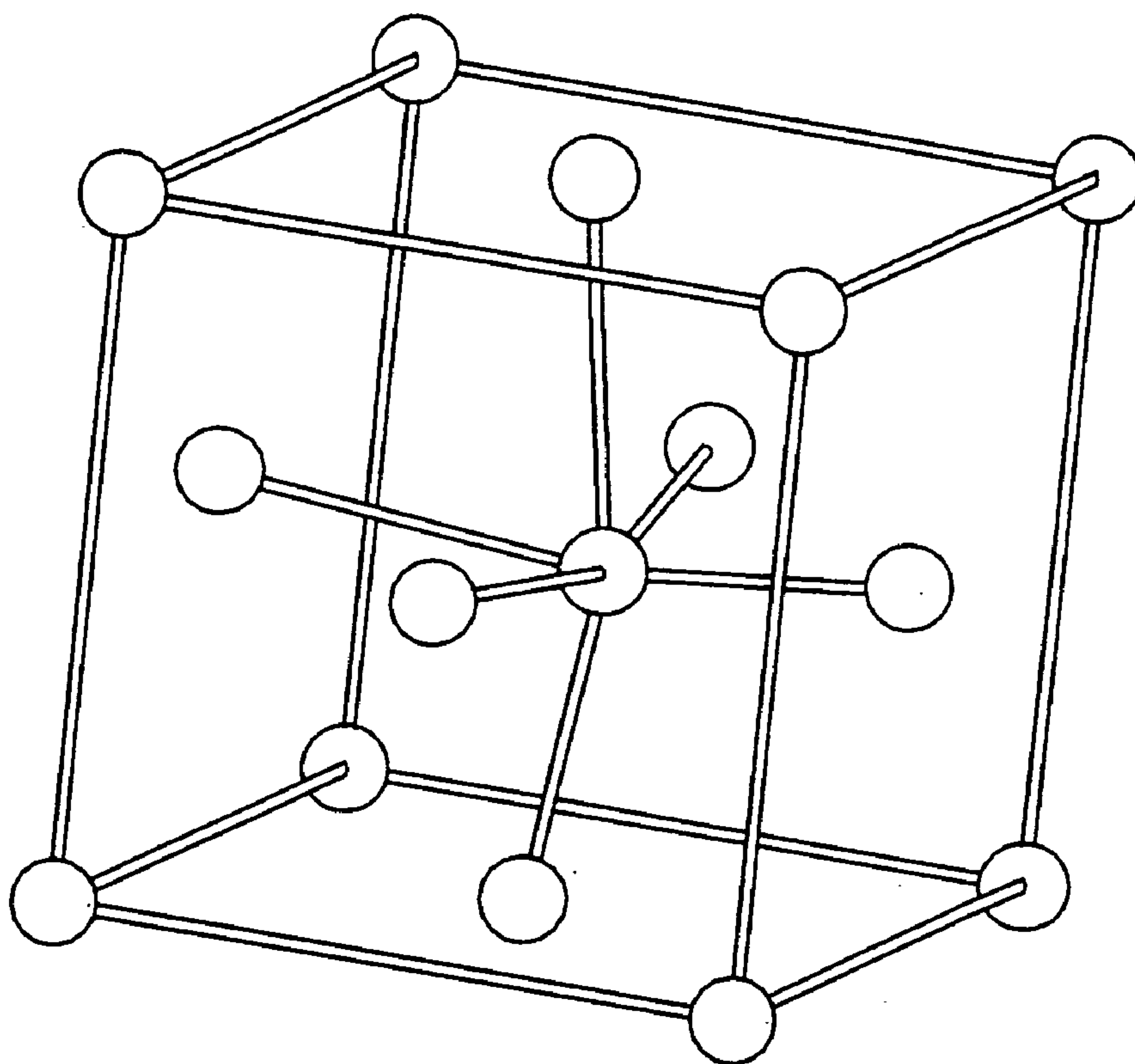
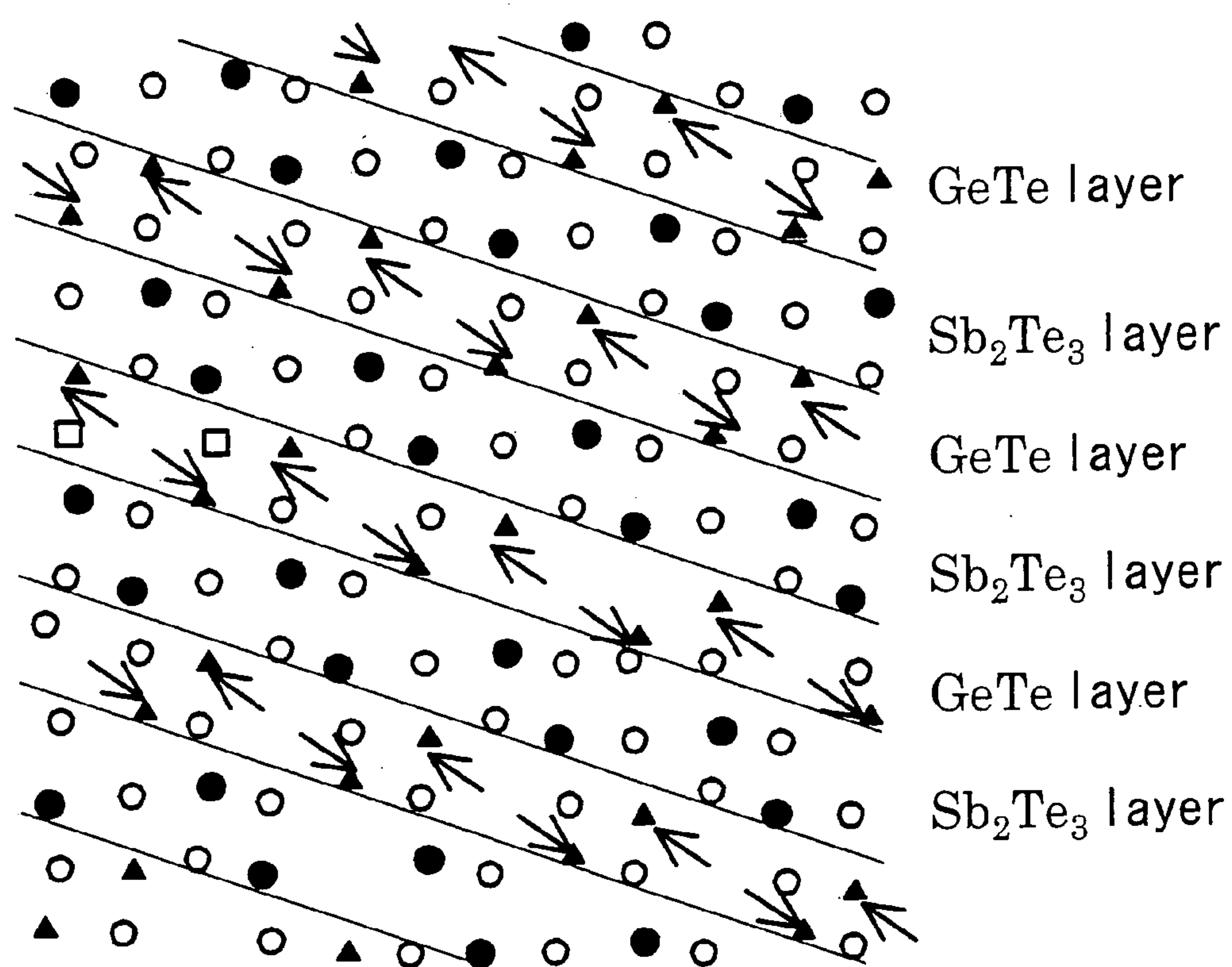


FIG. 4



White circle represents Te.
black circle represents Sb.
black triangle represents Ge.

SOLID MEMORY**TECHNICAL FIELD**

[0001] The present invention relates to a solid memory (phase-change RAM or PRAM) for recording and erasing, as data, a difference in electric resistance or optical characteristics which is caused between a crystalline state and an amorphous state of phase-transformation of a chalcogen compound consisting mainly of Te.

BACKGROUND ART

[0002] Recording and erasing of data in phase-change RAM have hitherto been performed based on a change in physical characteristics caused by primary phase-transformation between a crystalline state and an amorphous state of a chalcogen compound including Te which serves as a recording material, and phase-change RAM has been designed based on this basic principle (for example, see Patent Literature 1 below).

[0003] A Recording material used for recording and erasing data in a phase-change RAM is generally formed between electrodes by using a vacuum film formation method such as sputtering. Usually, a single-layered alloy thin film made by using a target made of a compound is used as such recording material.

[0004] Therefore, a recording thin film of 20-50 nm in thickness consists of a polycrystal but not a single crystal.

[0005] A difference in interfacial electric resistance between individual microcrystals influences uniformity in electric resistance values throughout a phase-change RAM as a whole, and causes variations in resistance values in a crystalline state (see Non Patent Literature 1 below).

[0006] Furthermore, it has been considered that about 10% change in volume generated in phase-transition between a crystalline state and an amorphous state causes individual microcrystals to have different stresses, and flow of material and deformation of an entire film restrict the number of times of readout of record (see Non Patent Literature 2 below).

[0007] Patent Literature 1: Japanese Patent Application Publication, Tokukai, No. 2002-203392 A

[0008] Non Patent Literature 1: supervisor: Masahiro Okuda, Zisedai Hikari Kiroku Gisyutsu to Zairyo (Technology and Materials for Future Optical Memories), CMC Publishing Company, issued on Jan. 31, 2004, p. 114

[0009] Non Patent Literature 2: supervisor: Yoshito Kadota, Hikari Disc Storage no Kiso to Oyo, edited by The Institute of Electronics, Information and Communication Engineer (IEICE), third impression of the first edition issued on Jun. 1, 2001, p. 209

[0010] Non Patent Literature 3: Y. Yamanda & T. Matsunaga, Journal of Applied Physics, 88, (2000) p. 7020-7028

[0011] Non Patent Literature 4: A. Kolobov et al. Nature Materials 3 (2004) p. 703

SUMMARY OF INVENTION

[0012] Technical Problem

[0013] Regarding a crystalline structure and an amorphous structure of a chalcogen compound including Te, the structural analysis has been made by X-ray and so on since the latter 1980s. However, since the atomic number of Te is next to that of Sb atoms which form the compound with Te and the number of electrons of Te is different from that of Sb atoms only by one, X-ray diffraction and electron ray diffraction

have hardly succeeded in discriminating Te from Sb. Consequently, detail of the crystalline structure of the chalcogen compound had been unclear until 2004.

[0014] Particularly, experiments have demonstrated that characteristics of a compound called GeSbTe (225 composition) and compositions prepared based on pseudobinary compound (a compound prepared based on GeTe—Sb₂Te₃, i.e. 225, 147 and 125 compositions), which have been already commercialized in the field of rewritable optical discs, are very excellent. However, it has been considered that crystalline structures of the compound and the compositions are sodium chloride structures with Te occupying a site (site (a)) which Na occupies and with Ge or Sb occupying a site (site (b)) which Cl occupies, and the way of occupying is random (see Non Patent Literature 3 above).

[0015] When structural analysis of a GeSbTe compound was made minutely by a synchrotron radiation orbit unit and so on, it was found that a chalcogen compound including Te took on a different aspect from a conventional structure in the following points (see Non Patent Literature 4 above).

[0016] 1. In a crystalline phase, orderings of Ge atoms and Sb atoms which occupy positions of Cl (site (b)) within NaCl-simple cubic lattices are not in a “random” state as having been considered so far, but positions of orderings of atoms are properly “determined”. Furthermore, lattices are twisted (see FIG. 1).

[0017] 2. In an amorphous state, orderings of atoms are not entirely random, but Ge atoms within crystalline lattices are positioned closer to Te atoms by 2Å from the center (though a bit misaligned and ferroelectric), and the amorphous state has a twisted structure while maintaining its atom unit (see FIG. 2).

[0018] 3. Restoration of the twisted unit enables high-speed switching to be repeated stably (see FIG. 3).

[0019] From the new principle of rewriting and readout, it was found that formation of a chalcogen compound including Te by the following method allows providing a new phase-change RAM capable of reducing interfacial electric resistance between individual microcrystals as much as possible, and of drastically increasing the number of times of repeated rewriting.

[0020] That is, it was found that a new phase-change RAM which can improve characteristics of a conventional phase-change RAM drastically is produced by forming GeSbTe compounds as superlattices including thin films of GeTe and thin films of Sb₂Te₃, causing Ge atoms within GeTe layers to be diffused over interfaces between the GeTe layers and Sb₂Te₃ layers by electric energy inputted in a memory so as to form “anisotropic crystal” which is a structure similar to a crystalline state (an erasing (recording) state) and returning Ge atoms stored in the interfaces to the original positions within GeTe layers by electric energy so as to return the structure to “an amorphous-like structure” which has an electric resistance value similar to that of a random structure referred to as an amorphous conventionally (a recording (erasing) state).

[0021] FIG. 4 shows a basic structure of this arrangement. The thickness of GeTe layers is about 0.4 nm, and the thickness of Sb₂Te₃ layers is about 0.5 nm. Generally, the thickness of each layer is preferably about 0.3-2 nm.

[0022] For example, in a case of forming a structure of the present invention by sputtering, it is preferable that a speed of film formation per time with respect to an electric power required for sputtering be measured in advance by using a

compound target including GeTe or Sb_2Te_3 (or by using a single target). By doing this, only controlling a time for the film formation allows easily forming a superlattice structure including these films.

[0023] In a case of forming a single-layered recording film with use of a compound target including composition of GeSbTe, movement of Ge atoms within a resulting microcrystal is random with respect to each microcrystal, and electric energy given in order to move Ge atoms does not have coherency, hence a lot of heat energy has to be wasted as entropy to a system thermodynamically, whereas in a superlattice structure of the present invention, movement of Ge atoms is made in a single direction (that is, having coherency) in a recording film as shown in FIG. 4, plentiful input energy is available for energy as a work, and amount of energy wasted as heat (entropy) can be reduced. Therefore, energy efficiency for performing phase-transformation is improved.

[0024] Furthermore, a change in volume (change in volume between a crystalline state and an amorphous state) caused by rewriting can be reduced by using an amorphous-like structure, and limiting a change in volume only to a uniaxial direction (that is, a work) allows operation of stably repeated rewriting without composition segregation.

[0025] Advantageous Effects of Invention

[0026] With the present invention, formation of a chalcogen compound including Te enables providing a new phase-change RAM which can reduce interfacial electric resistance between individual microcrystals as much as possible, make current value in recording data of a conventional phase-change RAM one-tenth or less, and increase the number of times of repeated rewriting in 2-3 digits or more.

BRIEF DESCRIPTION OF DRAWINGS

[0027] FIG. 1 shows a crystalline structure of Ge—Sb—Te alloy. Quadrangle represents Te, triangle represents Sb and circle represents Ge.

[0028] FIG. 2 shows an amorphous structure (short-distance structure) of Ge—Sb—Te alloy.

[0029] FIG. 3 shows a basic cell for switching of a phase-change RAM.

[0030] FIG. 4 shows a superlattice structure including GeTe and Sb_2Te_3 .

DESCRIPTION OF EMBODIMENTS

[0031] Best mode for carrying out the present invention is described below.

Example 1

[0032] A phase-separation RAM was formed using a basic technique of general self-resistance heating. TiN was used for an electrode. 20-layers of superlattices of GeTe and Sb_2Te_3 were laminated and the laminate was used as a recording film. The thickness of an entire recording film including the superlattices was 10 nm. The size of a cell was $100 \times 100 \text{ nm}^2$ square.

[0033] A voltage was applied on this device programmatically and current values in recording and erasing were measured. The results of measurements show that in recording,

the current value was 0.2 mA and the time of pulse was 5 ns, and in erasing, the current value was 0.05 mA and the time of pulse was 60 ns. The number of times of repeated recording and erasing at these current values was measured to be 10^{15} .

[0034] <Reference Example>

[0035] A phase-change RAM was formed using a technique of general self-resistance heating as in Example 1. A 20 nm single-layered film of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ was formed for a recording film. The size of a cell was $100 \times 100 \text{ nm}^2$ square. A voltage was applied on this device programmatically and current values in recording and erasing were measured. As a result, the current value in recording was 1.0 mA and the current value in erasing was 0.4 mA. Note that irradiation time of pulse was the same as in Example 1. The number of times of repeated recording and erasing at these current values was measured to be 10^{12} .

[0036] Industrial Applicability

[0037] In the present invention, formation of a chalcogen compound including Te enables providing a new phase-change RAM which can reduce interfacial electric resistance between individual microcrystals as much as possible, and can increase the number of times of repeated rewriting drastically.

1. A Solid Memory consisting mainly of tellurium (Te), electric characteristics thereof changing due to phase-transformation of a substance constituting the solid memory,

the substance serving as a material for recording and reproducing data, the material including a laminated structure of artificial superlattice structures made of thin films each including a parent phase which causes the phase-transformation.

2. The Solid Memory as set forth in claim 1, wherein: the laminated structure is made of alloy thin films including germanium (Ge) atoms and alloy thin films including stibium (Sb) atoms.

3. The solid memory as set forth in claim 1, wherein: a thickness of each of the alloy thin films including germanium (Ge) atoms and the alloy thin films including stibium (Sb) atoms ranges from 0.3 to 2 nm.

4. The solid memory as set forth in claim 2, wherein: data is recorded by causing the germanium (Ge) atoms to be anisotropically diffused from the alloy thin films including the germanium (Ge) atoms to interfaces between the alloy thin films including germanium (Ge) atoms and the alloy thin films including stibium (Sb) atoms.

5. The solid memory as set forth in claim 2, wherein: data is erased by causing germanium (Ge) atoms stored in interfaces between the alloy thin films including germanium (Ge) atoms and the alloy thin films including stibium (Sb) atoms to be anisotropically diffused to the alloy thin films including germanium (Ge) atoms.

6. The solid memory as set forth in claim 2, wherein: a thickness of each of the alloy thin films including germanium (Ge) atoms and the alloy thin films including stibium (Sb) atoms ranges from 0.3 to 2 nm.

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