3-6 Optical Thin Film Technology Used in the Terahertz Frequency

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The multi-layer optical films realize various functions such as wide-band anti-reflection coating, high reflection coating, low-pass filter, high-pass filter, band-pass filter, polarizing beam splitter, and non- polarizing beam splitter, etc. Although the multi-layer optical coatings are commonly used in light-wave regions (visible, near-infrared, and mid-infrared regions), it has not yet fully realized in the tera-hertz electromagnetic wave region (customarily defined as f = 0.3 - 10 THz, λ = 1000 - 30 μm). Single-layer coatings used at terahertz frequencies have realized by some methods, however, there has been almost no report on the fabrication method for the multi-layer coatings. Because each layer in the multi-layer structure must be as thick as several to several tens of micrometers, which is far thicker than coating used in optical regions. A method for manufacturing multi-layer optical coatings for optics used at tera-hertz frequencies has therefore been developed. The method forms a multi-layer structure, consisting of silicon and silicon-oxide layers, through plasma-enhanced chemical vapor deposition (CVD) using silane (SiH_4) and oxygen (O_2) as source gases. This method has lots of advantages over other methods. The details of the method and also the optical properties of a single layer anti-reflection coating and a four-layer wide-band anti-reflection coating on a germanium substrate are reported.

Keywords
Terahertz, Optical thin film, Plasma-enhanced chemical vapor deposition, Anti-reflection coating, Multi-layer coating/film

1 Introduction

The terahertz electromagnetic waves, located in a boundary region between radio and light waves, have recently attracted a great deal of attention. These electromagnetic waves get its name from its twelfth-power frequency region; “tera” is the prefix for this order of magnitude. Since tunable light sources and detectors have been unavailable for this region (100 GHz to 10 THz), its usage has been limited and for a long time has been referred to as an unused or undeveloped frequency region.

With recent developments in femtosecond laser technology and semiconductor device technology, it has become possible to generate and detect a terahertz electromagnetic wave pulse of a single cycle that contains frequency components in a wide range of the terahertz frequency region, using a method different from those of conventional light and radio wave technologies. As a result, new developments are being seen worldwide in various fields of applications, including material science, environmental measurement, and biotechnology.

Thus the problem of light sources and detectors have tentatively been resolved; however, various problems remain in the optical systems between these components, reducing overall efficiency of the developed systems.

One of the problems is to develop an appropriate optical thin-film technology. Optical thin-film technologies in the frequency regions of visible light and near-infrared light have nearly been perfected, contributing to the realization of highly efficient optical systems. On the other hand, optical thin-film technology in the terahertz frequency region remains insufficiently advanced and difficult to apply. This paper describes a convenient optical thin-film technology for the terahertz frequency region, equivalent to the technologies used in corresponding applications for the visible-light and near-infrared regions.

2 Optical thin film for terahertz frequencies and manufacturing requirements

Wavelengths of electromagnetic waves in the frequency region of terahertz (100 GHz to 10 THz) are 30 μm to 3 mm, from tens to several thousand times as long as wavelengths in the regions of visible and near-infrared light ($\lambda \sim 1$ μm); accordingly, an optical thin film in the terahertz region must be proportionally thicker. For example, consider a case in which a single-layer anti-reflection coating is formed on germanium (Ge; refractive index n = 4) at 1 THz ($\lambda = 300$ μm). Assuming SiO_2 (refractive index n = 2) is used as a film material, the required thickness ($\lambda/4$) becomes 37.5 μm. The thickness of this deposited film poses a primary problem in the manufacture of optical thin films for the terahertz frequency region.

There are a number of required characteristics for optical thin films to be used in the terahertz frequency region and a number of restrictions in the manufacturing method of such films, as follows.

(1) The thick film must be able to be manufactured within a practical time frame and at a reasonable cost. Widespread adoption of an optical thin film is contingent on these requirements over all others. Methods other than the CVD method described in this paper may be applied to create thin films for the terahertz region; however, many of these methods require significant amounts of time or involve prohibitive costs and thus cannot be put to widespread practical use.

(2) Two film materials that are transparent in the terahertz frequency region and that differ in refractive index must be layered with arbitrary thicknesses. Stacking of two such film materials enables the design and manufacture of optical thin films with a variety of functions (anti-reflection coatings, highly reflective coatings, various types of filters, polarizing/non-polarizing beam splitters, and more) on an arbitrary substrate material. To improve film quality, it is preferable to perform such manufacturing in an environment of reduced pressure (i.e., in a vacuum), enabling the switching of materials without exposing the manufacturing chamber to atmosphere.

(3) Stress in the film must be low, and must be lessened or canceled out in this region, just as with thin films in the visible-light and near-infrared regions. In the case of thick films in particular, this point must be taken into consideration. If the stress in the film is too large, the film will peel or crack, or the substrate itself will bend, crack, or otherwise deform.

(4) A uniform film must be manufactured on a substrate with excellent control exercised over film thickness, regardless of substrate shape. Most optical components besides flat mirrors employ curved surfaces, and may in some cases feature complicated shapes. The manufacturing process must therefore be applicable to any substrate shape.

(5) The film must offer mechanical durability and long-term stability, yet must be easy to handle. Since the developed optical thin films are likely to be exposed to a variety of environments, it is important for the films to excel in durability and stability. Since in particular optical thin films for the terahertz frequency region will see numerous applications at cryogenic temperatures,

it is important for the film to withstand temperature cycles between such cryogenic temperatures and normal room temperature.

The successful deposition of excellent optical thin films for the terahertz frequency thus essentially lies in finding a material and a manufacturing method satisfying the conditions (1) to (5) above.

3 Manufacture of SiO_2 film (refractive index n = 2) and Si film (refractive index n = 3.4) by plasma CVD

Plasma CVD (plasma-enhanced chemical vapor deposition), shown in Fig. 1, uses silane and oxygen and features the characteristics described below.

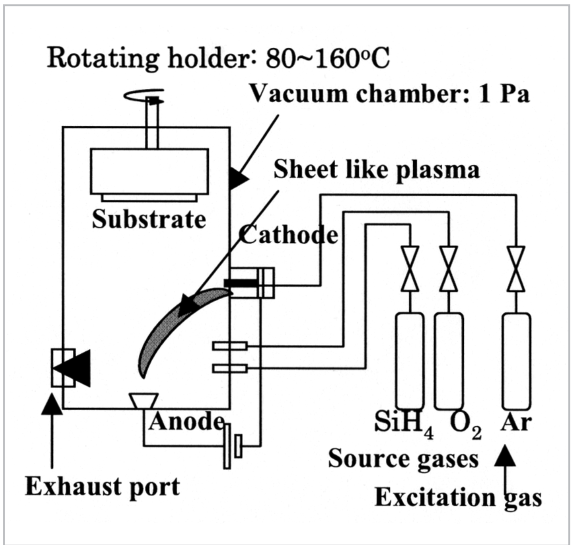

Fig.1 *Diagram of the plasma enhanced CVD*

(1) Allows for the deposition of an SiO_2 film and an Si film on a substrate at a relatively rapid deposition rate of approximately 5 μm/hour.
(2) Substrate temperature during film growth can be maintained as low as 80°C to 160°C; stress is thus suppressed in the film.
(3) A high-quality film can be formed with no impurities, as the method uses high-purity gases as raw materials and decomposes these gases in high-density plasma for film deposition.
(4) Change in film type can be performed through control of the oxygen supply by opening and shutting a valve, without exposing the reactor furnace to the atmosphere. This allows for the convenient formation of a multi-layer film. Moreover, films each consisting of a mixture of SiO_2 and Si (refractive index n = 2 to 3.4) can be manufactured through partial adjustment of the oxygen pressure using the valve.
(5) Hardness and environmental resistance of both SiO_2 and Si films facilitate use in a range of applications.
(6) The CVD process allows for the manufacture of highly uniform films with excellent control of film thickness, regardless of substrate shape.

It can be concluded that this CVD process represents a promising method for the manufacture of optical thin films in the terahertz frequency region, as the process may be seen to satisfy a substantial portion of the necessary conditions described in II above. Table 1 summarizes references[2]-[7] and illustrates a comparison of this method with various previous methods of manufacturing optical thin films for the terahertz frequency region. These earlier methods may be viewed as less suitable for a number of reasons, as follows.

Vacuum deposition of SiO_2 and Si is slow in terms of film deposition (approximately 1 μm/hour), and requires the supply of additional raw materials during the film-formation process, as it is impossible to ensure sufficient volume of the raw material crucible at the outset, for example. The TEOS-CVD[2] process has a number of drawbacks: for example, it does not permit construction of a multilayer structure, and the film-formation temperature must be high. Since the target thickness is relatively large, it would be possible to affix a film material on the substrate with an optical adhesive and to grind this material to create an anti-reflection coating. However, this method[6] is considered to be too time-con-

Table 1 *The table compares the SH_4 / O_2 – plasma enhanced CVD with other methods.*

Methos	Refractive index	Fabrication temperature	Residual stress	Time for fabrication	Uniformity & Controllabirity	Multi-layer structure	Long-term stability	Restriction on substrate shape
Si / SiO_2 evapolation	**2 & 3.4**	~ 200 °C	High	Long	O	O	O	None
TEOS-CVD[2]	2	> 200 °C	High	**Short**	O	X	O	None
Attach & polish[6]	**Selectable**	**Room temperature**	**Low**	Long	O	O	X	Exist
Paste plastic films[3-5]	~1.5	**Room temperature**	**Low**	Short	X	O	X	Exist
SH_4 / O_2 – CVD[7]	**2 ~ 3.4**	**160 °C**	**Low**	**Short**	O	O	O	None

suming and costly in terms of applications to multi-layer films and optical devices (with the exception of planar surface devices). The method of affixing a plastic film on the substrate[3]-[5] presents problems in terms of film thickness, uniformity, limitations on the shape of the optical device, and long-term instability, among others.

4 Applicable terahertz frequencies with plasma CVD optical thin films

The optical constants (1 to 10 THz) of SiO_2 (glass) and Si are shown in Fig. 2[1]. The respective refractive indices are approximately 2 and 3.4, and remain at these levels at 1 THz or less[8]. Although the absorption coefficient of SiO_2 becomes larger at high frequencies, variation in the absorption coefficient is limited to several percent as long as the total film thickness of the SiO_2 element is within a range of several times the thickness of $\lambda/4$. On the other hand, the absorption coefficient of Si becomes larger at low frequencies. This may pose a problem at frequencies of 1 THz or less, beyond the frequency region shown in the figure. This is due to Drude-type absorption caused by free carriers in the Si. At cryogenic temperatures (approximately 4 K), the carriers are frozen out, and thus it can be assumed that this absorption will disappear. Therefore, it can be said that the application frequency region of an optical thin film fabricated using this method is, broadly speaking, 1 THz to 10 THz at room temperature and 0.1 THz to 10 THz at cryogenic temperatures, although this will depend on the specific substrate material employed.

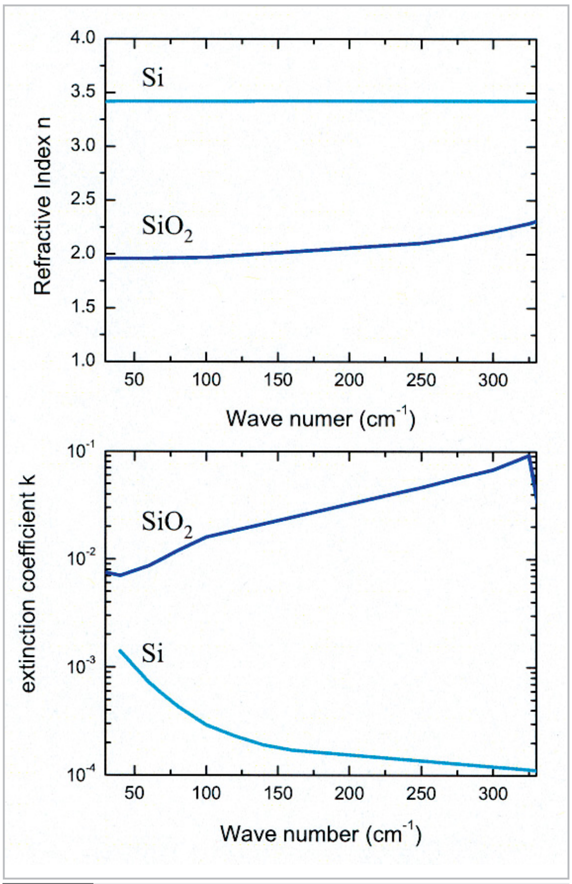

Fig.2 *Optical constants of Si and SiO_2*

5 Results of experimental manufacture

(1) Single layer coating[7]

A single layer of SiO_2 anti-reflection coating was deposited by the plasma CVD method on a substrate of germanium (Ge), a material used for detectors and lasers in the terahertz frequency region. The Ge single-crystal substrate used featured a diameter of 21 mm, a thickness of 1,989.5 μm, and resistivity of 44.9 Ω-cm. An SiO_2 film was deposited to a thickness of 20.9 μm on one surface of the substrate by the plasma CVD method ($SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$) at a reactor furnace pressure of 1 Pa and a substrate temperature of 160°C. At this time, target deposition thickness was 20.4 μm. This thickness was selected so that the center wavelength of the anti-reflective property would be 160 μm (62.5 cm^{-1}). Error in achieving target film thickness was 2.5%. Figure 3 shows the measurement results for the transmittance of the Ge substrate with this single-surface anti-reflection coating using a Fourier transform infrared interferometer (BomemDA-8). The detector used in measurement was a liquid-helium-cooled Si bolometer. The bolometer was equipped with a low-pass filter with a cutoff frequency of 140 cm^{-1}. In order to avoid the influence of water vapor, a sample was disposed in a vacuum (66.7 Pa = 0.5 torr or less). A mercury lamp was used for the light source, and a Mylar film 12-μm thick was used for the beam splitter. Measurement resolution was 0.01 cm^{-1}. It can be seen from Fig. 3 that the amplitude of the interference pattern caused by reflection from the surface and the back of the Ge substrate reaches minimum at frequencies from 55 cm^{-1} to 60 cm^{-1}. It was therefore concluded that the film functioned effectively as an anti-reflection coating at these frequencies.

The shift of the center frequency of the anti-reflective property away from the design value is partly due to film thickness and partly due to the difference between the refractive index of the SiO_2 film deposited by the CVD method and the actual design value. Here, the film deposited by the CVD method is analyzed assuming that the film is a mixture of SiO_2 and Si. Representing the mixture as SiO_x (where “x” denotes the degree of mixing), it was found that the film deposited by the CVD method consisted of $SiO_{1.81}$; the refractive index n_m was 2.10, the center frequency of the anti-reflective property λc was 175.4 μm (57.0 cm^{-1}), and the reflectivity at λc, R, was 2×10^{-3}. The transmittance of 0.549 (at λc) calculated using this analytical value agreed well with the actually measured value of 0.547; therefore, a film deposited by the CVD method may be treated as a mixture of SiO_2 and Si, and it is safe to say that absorption in the film is negligible for practical purposes. The reflectance obtained in this case was as low as 1/180 of the Fresnel reflectivity, which was 0.36.

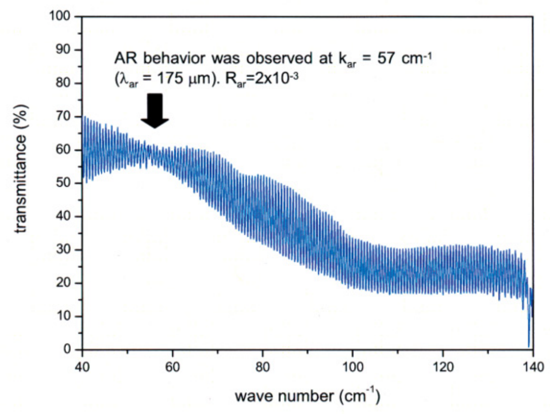

Fig.3 *This figure shows transmittance spectrum of the Ge wafer (1989.5 μm thick) with an AR coating (a 20.9-μm-thick SiO_2 layer) on one surface. The reflectivity of 2×10^{-3} has successfully demonstrated at k = 57 cm^{-1}.*

(2) Multi-layer coating

A four-layer wide-band anti-reflection coating consisting of two kinds of films (SiO_2 film and Si film) was manufactured on a Ge substrate by the CVD method. The target multilayer structure consisted of 7 μm Si / 3 μm SiO_2 / 2 μm Si / 11 μm SiO_2, formed, in that order, on the Ge substrate. First, the above-mentioned multilayer structure was manufactured on one surface of a substrate 4-

mm thick; this sample was then sliced and separated into a Ge substrate approximately 2.2-mm thick and a Ge substrate approximately 0.9-mm thick featuring a multi-layer film on one surface. Each cutting surface was optically polished to form a plate consisting of a parallel plane. Transmittance of each substrate was measured as in the single-layer case. Measurement resolution was set to 4.0 cm^{-1}. Transmission measurement results for a Ge substrate approximately 2.2-mm thick was used as a reference when deriving the transmission value for the multi-layer film. After measuring transmittance, a cross-section of the multi-layer film was observed with a scanning electron microscope (SEM) and subject to component analysis by energy dispersive X-ray spectroscopy (EDS). The EDS spatial resolution was on the order of 1 μm.

Figure 4 shows an SEM view of the cross-section, and Fig.5 shows the results of EDS observation. Figure 4 indicates a layer configuration of 6.8 μm Si / 3.2 μm SiO_2 / 1.8 μm Si / 11.8 μm SiO_2 and that the boundaries of layers are well-defined. It can be seen in Fig. 5 that oxygen has been included in the Si layer, which is considered to be a film consisting of a mixture of SiO_2 and Si. Representing the degree of mixing as in the case of the single layer, the structure of the obtained four-layered film is 6.8 μm $SiO_{0.26}$ / 3.2 μm $SiO_{1.88}$ / 1.8 μm $SiO_{0.50}$ / 11.8 μm $SiO_{1.81}$. Note that it is assumed that the 11.8-μm layer features the same degree of mixing as seen in the single layer.

Figure 6 shows the calculated transmittance value of the target structure st1 (7 μm Si / 3 μm SiO_2 / 2 μm Si / 11 μm SiO_2); the calculated transmittance value of structure st2, in which the measured values are taken as layer thicknesses (6.8 μm Si / 3.2 μm SiO_2 / 1.8 μm Si / 11.8 μm SiO_2); and the calculated and measured transmittance values of structure st3 obtained above (6.8 μm $SiO_{0.26}$ / 3.2 μm $SiO_{1.88}$ / 1.8 μm $SiO_{0.50}$ / 11.8 μm $SiO_{1.81}$). Only a small difference is seen in the calculated values for structure st1 and structure st2. These results indicates that the CVD method provides sufficient control of film thickness in the THz frequency region.

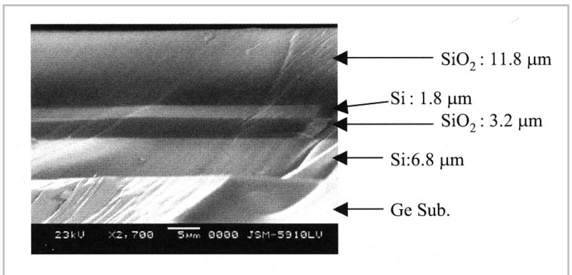

Fig.4 *The SEM viewgraph of the cross section of four layer AR coating*

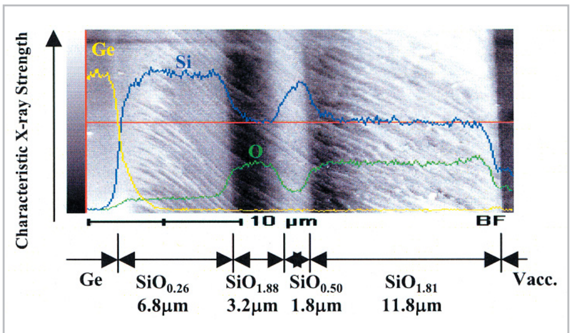

Fig.5 *The cross-sectional SEM viewgraph of the four layer AR coating with the results of EDS analysis*

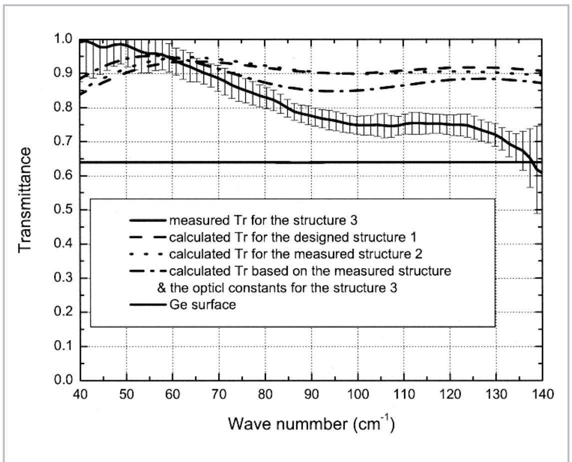

Fig.6 *The calculated transmittance for the structure 1, 2, and 3 are shown by dotted lines. Black solid lines show the measured transmittance for the structure 3 and for the Ge surface.*

The measured transmittance of the target structure is lower than the calculated transmittance at frequencies of 60 cm^{-1} or higher and higher than the calculated amount below this frequency. It is thought that this is not due to film thickness but rather to the difference between the actual refractive index of each layer and the respective design values. The calculated values for the obtained structure st3 show the same tendencies as the measured values, but do not coincide with the latter quantitatively. However, since the measured transmittance values are larger than the Ge surface transmittance of 0.64 over the given frequency region, we may conclude that the structure acts as an effective wide-band anti-reflection coating. We believe that differences between design and measured values can be reduced to negligible levels through experimental refinement of manufacture (composition) and measurement (transmittance).

These results have demonstrated that it possible apply the plasma CVD method to manufacture a dielectric multi-layer film that will prove effective in the terahertz frequency region. Although the methods of experimental manufacture and measurement need to be refined to ensure that the desired characteristics are obtained, it has been verified that this method allows for the manufacture of various types of optical thin films in the terahertz frequency region (anti-reflection coatings, highly reflective coatings, various types of filters, polarizing beam splitters, etc.) at practical cost and within a reasonable period of time.

(3) Anti-reflection coating on sapphire substrate

We are currently in the process of experimental manufacture of an anti-reflection coating on a sapphire substrate designed for use in an ambitious international project referred to as the “Atacama Large Millimeter/Submillimeter Array” (ALMA) (http://www.nro.nao.ac.jp/%7Elmsa/), conducted jointly with the ASTE group of the Advanced Technology Center at the National Astronomical Observatory of Japan. An SiO_x (x ~ 1.8) single-layer film 47.1 μm thick was deposited on a sapphire substrate by the plasma CVD method. Through evaluation of transmittance characteristics at room temperature (300 K) and at cryogenic temperatures (5 K), the single layer was confirmed to exhibit excellent anti-reflective characteristics at 25 cm^{-1}. No cracks or peeling attributable to the temperature cycle were observed, confirming the effectiveness of the CVD method in terms of temperature. We are now designing a target structure (January 2004) aimed at establishing a wider frequency region with sufficient anti-reflective properties through adoption of a multi-layer film structure.

6 Conclusions

We have proven that a variety of optical thin films can be manufactured to function effectively in the terahertz frequency region via the plasma CVD method, using silane and oxygen as raw material gases, presenting actual examples of experimental manufacture of a single-layer anti-reflection coating and a wide-band multi-layer anti-reflection coating.

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